

Available online at www.sciencedirect.com



Lithos 80 (2005) 363-386



www.elsevier.com/locate/lithos

Sn-polymetallic greisen-type deposits associated with late-stage rapakivi granites, Brazil: fluid inclusion and stable isotope characteristics

Jorge S. Bettencourt^{a,*}, Washington B. Leite Jr.^b, Claudio L. Goraieb^c, Irena Sparrenberger^a, Rosa M.S. Bello^a, Bruno L. Payolla^d

^aInstituto de Geociências, Universidade de São Paulo, São Paulo, SP, Brazil ^bInstituto de Geociências e Ciências Exatas, Universidade Estadual Paulista, Rio Claro, São Paulo, SP, Brazil ^cInstituto de Pesquisas Tecnológicas, São Paulo, SP, Brazil ^dEletronorte S/A, Brasília, Distrito Federal, DF, Brazil

> Received 21 May 2003; accepted 9 September 2004 Available online 21 November 2004

Abstract

Tin-polymetallic greisen-type deposits in the Itu Rapakivi Province and Rondônia Tin Province, Brazil are associated with late-stage rapakivi fluorine-rich peraluminous alkali-feldspar granites. These granites contain topaz and/or muscovite or zinnwaldite and have geochemical characteristics comparable to the low-P sub-type topaz-bearing granites. Stockworks and veins are common in Oriente Novo (Rondônia Tin Province) and Correas (Itu Rapakivi Province) deposits, but in the Santa Bárbara deposit (Rondônia Tin Province) a preserved cupola with associated bed-like greisen is predominant. The contrasting mineralization styles reflect different depths of formation, spatial relationship to tin granites, and different wall rock/fluid proportions. The deposits contain a similar rare-metal suite that includes Sn (\pm W, \pm Ta, \pm Nb), and base-metal suite (Zn–Cu–Pb) is present only in Correas deposit. The early fluid inclusions of the Correas and Oriente Novo deposits are (1) low to moderatesalinity (0–19 wt.% NaCl eq.) CO₂-bearing aqueous fluids homogenizing at 245–450 °C, and (2) aqueous solutions with low CO₂, low to moderate salinity (0-14 wt.% NaCl eq.), which homogenize between 100 and 340 °C. In the Santa Bárbara deposit, the early inclusions are represented by (1) low-salinity (5–12 wt.% NaCl eq.) aqueous fluids with variable CO_2 contents, homogenizing at 340 to 390 °C, and (2) low-salinity (0-3 wt.% NaCl eq.) aqueous fluid inclusions, which homogenize at 320-380 °C. Cassiterite, wolframite, columbite-tantalite, scheelite, and sulfide assemblages accompany these fluids. The late fluid in the Oriente Novo and Correas deposit was a low-salinity (0-6 wt.% NaCl eq.) CO2-free aqueous solution, which homogenizes at (100-260 °C) and characterizes the sulfide-fluorite-sericite association in the Correas deposit. The late fluid in the Santa Bárbara deposit has lower salinity (0-3 wt.% NaCl eq.) and characterizes the late-barren-quartz, muscovite and kaolinite veins. Oxygen isotope thermometry coupled with fluid inclusion data suggest hydrothermal activity at 240-450 °C, and 1.0-2.6 kbar fluid pressure at Correas and Oriente Novo. The hydrogen isotope composition of breccia-greisen, stockwork, and vein fluids

* Corresponding author. Tel.: +55 11 3091 4205; fax: +55 11 3091 4258. *E-mail address:* jsbetten@usp.br (J.S. Bettencourt).

 $(\delta^{18}O_{quartz}$ from 9.9% to 10.9%, δD_{H_2O} from 4.13% to 6.95%) is consistent with a fluid that was in equilibrium with granite at temperatures from 450 to 240 °C. In the Santa Bárbara deposit, the inferred temperatures for quartz-pods and bed-like greisens are much higher (570 and 500 °C, respectively), and that for the cassiterite-quartz-veins is 415 °C. The oxygen and hydrogen isotope composition of greisen and quartz-pods fluids ($\delta^{18}O_{qtz-H_2O}=5.5-6.1\%$) indicate that the fluid equilibrated with the albite granite, consistent with a magmatic origin. The values for mica ($\delta^{18}O_{mica-H_2O}=3.3-9.8\%$) suggest mixing with meteoric water. Late muscovite veins ($\delta^{18}O_{qtz-H_2O}=-6.4\%$) and late quartz ($\delta^{18}O_{mica-H_2O}=-3.8\%$) indicate involvement of a meteoric fluid. Overall, the stable isotope and fluid inclusion data imply three fluid types: (1) an early orthomagmatic fluid, which equilibrated with granite; (2) a mixed orthomagmatic-meteoric fluid; and (3) a late hydrothermal meteoric fluid. The first two were responsible for cassiterite, wolframite, and minor columbite–tantalite precipitation. Change in the redox conditions related to mixing of magmatic and meteoric fluids favored important sulfide mineralization in the Correas deposit. © 2004 Elsevier B.V. All rights reserved.

Keywords: Rapakivi granite; Greisen deposits; Fluid inclusions; Stable isotopes; Brazil

1. Introduction

Proterozoic rapakivi granites in Brazil range in age from 1.88 to 0.59 Ga and are found in an anorogenic tectonic setting in the Amazonian craton (1.88-0.97 Ga) and the Tocantins Province (1.77–1.55 Ga), and in a post-orogenic tectonic setting in the Itu Rapakivi Province, which is a part of the Central Mantiqueira Province (800-540 Ma) (Almeida et al., 1981; Vlach et al., 1990; Wernick, 1992; Wernick et al., 1991; Ulbrich et al., 1991; Pimentel et al., 1991; Dall'Agnol et al., 1999; Bettencourt et al., 1995, 1999). Important Sn-polymetallic deposits are associated with some of them. The Rondônia and Pitinga provinces in the Amazonian craton produce tin with a total output of ~500,000 t Sn in concentrate. The current output comes mainly from the Pitinga Mining District (~230,000 t Sn by 2002), and the Bom Futuro Mine in the Rondônia Tin Province (170,000 t Sn by 2002).

Despite the progress achieved in the last few years, the magmatic-metallogenetic history of the rapakivi granites in Brazil is far from being fully understood and fundamental questions still require answers, before their origin, evolution, and relation with associated mineral deposits can be satisfactorily deciphered. The purpose of this work is to combine fluid inclusion and stable isotope data to estimate the temperature, pressure and source of fluids, and to present a comparative study of the Sn-polymetallic greisen-type deposits. These include the Correas deposit in the Itu Rapakivi Province, and the Santa Bárbara and Oriente Novo deposits in the Rondônia Tin Province.

2. Geologic setting

2.1. Itu Rapakivi Province

The Itu Rapakivi Province in the State of São Paulo, SE Brazil comprises a dozen post-collisional granite batholiths and stocks, which cross-cut the low to medium-grade metamorphic rocks of the Ribeira Fold Belt. The granites have U-Pb, Rb-Sr and K-Ar ages in the range of 0.6-0.5 Ga, and thus overlap and follow the late Brasiliano calc-alkaline magmatism (Janasi and Ulbrich, 1991; Campanha and Sadowski, 1999; Gimenez Filho et al., 2000; Prazeres Filho, 2000). Their composition varies from subalkaline to almost alkaline granitoids, and they are nearly similar to the Finnish rapakivi granites (Wernick et al., 1997). Some of them are locally associated with mineral deposits in the Itu Complex (W), Correas massif (Sn, W, Zn, Cu, Pb), and São Francisco massif (Sn, W, fluorite).

2.2. Rondônia Tin Province

The Rondônia Tin Province comprises mainly Paleo- to Mesoproterozoic medium- to high-grade metamorphic rocks, locally overlain by low-grade to underformed supracrustal sequences (Scandolara et al., 1999; Payolla et al., 2002). Six discrete episodes of magmatism have affected these rocks, and are represented by at least seven rapakivi suites with ages between 1.60 and 0.97 Ga (Bettencourt et al., 1999). Important Sn-polymetallic deposits are associated with at least the three youngest suites: the São Lourenço-Caripunas Intrusive Suite (ca. 1.31 Ga), the Santa Clara Intrusive Suite (1.08-1.07 Ga), and the Younger Granites of Rondônia (1.00-0.97 Ga). The Santa Clara Intrusive Suite and the Younger Granites of Rondônia are found in the east-central part of the Rondônia Tin Province and show petrographic, geochemical and metallogenetic similarities (Leite et al., 2000, 2001). These suites are composed of several early- and late-stage intrusions. The latestage intrusions are volumetrically minor, and comprise two rock groups: (1) a metaluminous to peralkaline group composed mainly of hornblende $(\pm pyroxene, \pm biotite)$ alkali feldspar syenite and microsyenite, trachyandesite, and trachyte, as well as biotite (±sodic amphibole) alkali feldspar granite and rhyolite; and (2) a peraluminous group formed by biotite-alkali feldspar granite, alaskite, Li-mica (±topaz) alkali-feldspar granite and Li-mica (±topaz) rhyolite porphyry (ongonite). The Snpolymetallic greisen-type deposits are closely associated with these peraluminous rocks in both suites, such as in the Oriente Novo massif of the Santa Clara Intrusive Suite, and in the Santa Bárbara massif of the Younger Granites of Rondônia.

3. Methods

Microthermometry and Raman spectroscopy were carried out at the Instituto de Geociências, Universidade de São Paulo, Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista, and Instituto de Ciências Exatas, Universidade Federal de Minas Gerais. Microthermometry was performed using a CHAIXMECA MTM-85 stage and a Linkam THMS 600 heating-freezing stage fitted with a video system. Heating rates of 2 $\,^\circ\text{C/min}$ were used for Th determinations. The CHAIXMECA and Linkam THMS 600 stages were calibrated to the Merck Signotherm standard for low temperatures and Merck MSP standard for high temperatures; SYN FLINC synthetic inclusions (comercially available from FLUIDS, Denver, CO, USA) were also used. Precision estimates are ± 0.2 °C for temperatures between -60 and 25 °C, and ± 5 °C between 100 and 400 °C. The bulk composition of the fluid inclusions were calculated considering eutetic temperatures (Davis et al., 1990), ice, chlatrate and CO₂ melting temperatures and Raman spectrometry (Bodnar, 1993; Potter et al., 1978; Collins, 1979; Diamond, 1994; Heyen et al., 1982). The FLINCOR software (Brown, 1989) was used for isochore calculations (Correas and Oriente Novo deposits). This software is based on the Brown and Lamb (1989) and Bowers and Helgeson (1983) equations for the systems $H_2O+NaCl$ and H_2O+CO_2+NaCl , respectively. Raman spectrometry was performed on a micro-Raman type DILOR XY.

Oxygen analyses of granite whole-rock and mineral separates from granite, quartz-vein, stockwork and greisen were carried out using the conventional fluorination technique (Clayton and Mayeda, 1963; Mcaulay et al., 2000) at Krueger Geochron Laboratories, Cambridge, OH, USA, and at the Scottish Universities Environmental Research Center (SUERC), East Kilbride, Scotland. Hydrogen isotope analyses were carried out by thermal degassing of minerals at 1400 °C (Fallick et al., 1993). Hydrogen was produced from water vapor using a chromium (Donnelly et al., 2001) or the conventional uranium furnace. Isotopic data are reported in the standard δ notation as per mil (‰) deviation from the Vienna SMOW standard for oxygen and hydrogen. The analytical precision is about $\pm 0.2\%$ for oxygen and $\le 0.5\%$ for hydrogen.

4. Correas deposit (Itu Rapakivi Province)

4.1. Geologic outline

The Correas massif is a post-tectonic, ellipsoid shaped, NE–SW trending stock (5 km²), with ages of 603 ± 7 Ma (Rb–Sr), and 619 ± 11 Ma (U–Pb, monazite) (Goraieb, 2001). It comprises five units: biotite granite, biotite–muscovite granite, microgranite, topaz–muscovite–albite granite, and layered marginal pegmatite. The early-stage intrusions are metaluminous monzogranite to syenogranite. The late phases are evolved topaz–muscovite–albite syenogranites and alkali feldspar granites.

The tin-bearing topaz–muscovite–albite granite is porphyritic, containing muscovite, phengite and drop-like quartz phenocrysts. Granophyric and snowball textures are common. Laths of albite, nonperthitic microcline, quartz and muscovite are the primary minerals. Typical accessory minerals are topaz, cassiterite, fluorite, zircon, monazite, xenotime, iron oxides, sphalerite and pyrite (Goraieb, 2001). This tin granite facies is slightly peraluminous, has high SiO₂, Al₂O₃, Na₂O, F and Rb contents, and is poor in MgO and TiO₂. The REE pattern is characterized by slight enrichment of HREE and a marked negative Eu anomaly. The mineralogy, geochemical and isotope data point to a magmatic origin, and they are comparable to the low-P, topaz granite sub-type (cf. Taylor, 1992; Taylor and Fallick, 1997).

4.2. Mineralization

The Correas primary (Sn, W, Zn, Cu, Pb) deposit is dominantly a pipe-shaped stockwork and/or brecciatype deposit, hosted by schists, calc-silicate rocks, and granitic/granodioritic gneisses. Ore reserves are 5000 t Sn-in concentrate at 0.20% Sn and 1400 t W at a depth of 60 m. The tin deposit is represented by six ellipsoid or lens-shaped pipe-like ore bodies, which plunge steeply above the granite underlying cupola (Fig. 1). They are up to 50 m thick, at least 60 m deep, and trend WNW–ESE. The maximum width of the greisen zones is 150 m. These are genetically related to the topaz–muscovite–albite granite, and probably formed during hydraulic fracturing. This led to the following styles of mineralization: (a) cassiterite and wolframitebearing pipe-like quartz-stockwork veins and veinlets (ore bodies 1 and 4; Fig. 1); (b) pipe-shaped breccia (ore-bodies 2 and 3; Fig. 1) represented by tabular steeply dipping greisen columns developed within gneissic and calc-silicatic rocks. It includes cassiterite and minor wolframite mica-topaz-quartz-greisen, mica greisen, topaz-fluorite-mica greisen, milky quartz pods and veins. Breccia infill consists of sulfides (pyrite, chalcopyrite and sphalerite, followed by minor chalcocite, pyrrhotite as well as trace amounts of sellaite, stannite, and bismuthinite), and fluorite associated with mica. The greisens also include late fluorite and sericite, and are associated with cassiterite-rich topaz veins and veinlets (Fig. 2).

4.3. Fluid inclusions

Fluid inclusions were studied mainly in quartz crystals from the quartz stockwork and breccia greisen, and in topaz and quartz from mica-topazquartz greisen. All samples were taken from drillcores of the ore bodies 1 and 4, and from outcrops of the marginal pegmatite. Microthermometric studies were performed on unmodified primary fluid inclusions (10–20 μ m) with usually rounded, seldom irregular, negative crystal morphology. The primary fluid inclusions are randomly distributed in the inner part or along the growth-planes of the topaz and quartz. Three main types of fluid inclusions were distinguished based on morphology, composition, volume percentage of vapor phase, mode of homog-



Fig. 1. Schematic geological map and styles of mineralization of the Correas (Sn, W, Zn, Cu, Pb) deposit as shown by the cross-sections through the LS-03 and LS-04 ore bodies. Abbreviations: Tp-topaz; Ms-muscovite. Location relative to Brazil is shown in left panel.



Fig. 2. Simplified paragenetic and mineral formation stage diagram for the Correas and Oriente Novo deposits.

enization (liquid/vapor/critical), and the presence of accidental minerals. Different fluid inclusions types are found together in the same samples. They have highly variable salinities, compositions, bulk densities of the carbonic phase, and show distinct homogenization characteristics. Microthermometric data are summarized in Table 1.

Type I fluid inclusions $(CO_2\pm CH_4-H_2O-NaCl-KCl-FeCl_2\pm CaCl_2)$ were observed in quartz from quartz-stockwork, breccia-greisen, and the mica-

topaz-quartz greisen. The salinities are in the range of 0–19 wt.% NaCl eq., and the predominant volumetric proportion of the CO₂ phase varies from 20 to 90 vol.%. Homogenization temperature (Th) from primary inclusions into the H₂O or CO₂ phases in quartz has a range of 245–450 °C (Table 1). Type II (H₂O–NaCl–KCl–FeCl₂±CaCl₂) inclusions are observed in quartz-stockwork and breccia greisen. They are two-phase, essentially aqueous inclusions with little CO₂, and the vapor bubble occupies 10–30 vol.%. The salinities are

Table 1					
Summary of fluid	inclusion	data	from	Correas	deposit

Stage	Morpho-structural types	Mineral	Type of fluid inclusion	Tm _{CO2} (°C)	<i>T</i> _e (°C)	Th_{CO_2} (°C)	V _{CO2} (%)	Tm _{CL} (°C)	Salinity (wt.% NaCl eq.)	Th (°C)
Post-magmatic	Quartz stockwork	Qtz	Туре І	-61.6 to -57.7	-47.6 to -32.4	3.3 to 29.3	20–99	-2.6 to 9.1	2 to 18	250 to 400
			Type II		-43.7 to -31.6		10–30	4.5 to 9.0	1 to 10	170 to 250
			Type III		-38.1 to -27.3		5–20	-3.5 to -0.8	1 to 6	100 to 150
	Breccia greisen	Qtz	Type I	-60.4 to -59.0	-37.4 to -28.6	-50.5 to 22.4	20–99	-5.0 to 10.2	2 to 19	260 to 450
			Type II		-35.9 to -29.8		10–30	6.7 to 10.9	0 to 4	130 to 230
			Type III		-39.9 to -28.7		5–20	−7.6 to −0.1	0 to 11	110 to 240
	Mica-tp-qtz greisen	Qtz	Type I	-64.6 to -57.8	_	-27.6 to 30.4	90–99	-6.2 to 6.3	_	-
	-		Type III		−34.7 to −29.7		5–20	-4.0 to -2.6	1 to 6	180 to 260
	Stockscheider	Qtz	Type I	-57.2 to -58.5	-33.3 to -38.4	15.7 to 29.5	5–95	3.1 to 7.5	5 to 12	245 to 420
		Тр	Type I	-57.0 to -58.1	-32.9 to -39.0	27.6 to 29.0	15-50	3.8 to 5.6	8 to 11	270 to 330

Abbreviations: Qtz—quartz; Tp—topaz; V_{CO_2} —CO₂ volumetric proportion; Th_{CO2}—CO₂ homogenization temperature; Tm_{CO2}—CO₂ melting temperature; Tm_{CL}—chlatrate melting temperature; Te—eutectic temperature; Th—homogenization temperature.

lower, varying from 0 to 10 wt.% NaCl eq., and Th into the liquid phase lies between 130 and 250 °C. Type III (H₂O–NaCl±KCl) late fluid inclusions, observed in quartz-stockwork, breccia, greisens and mica-topaz greisen, are two-phase, essentially aqueous solutions without CO₂, showing low salinities in the range of 0– 11 wt.% NaCl eq., and L/V of 5–20 vol.%. Homogenization of the inclusions takes place at temperatures of 100–260 °C.

The trapping P-T conditions of the observed fluids (Table 2) vary from 440 to 300 °C at 2.6–1.3 kbar, and were obtained through the intercept of isochores of the CO₂-rich and H₂O-rich fluids, considering that Type I

and Type II fluid inclusions exhibit some fluid unmixing features (Fig. 3A–C). This is indicated by the occurrence of CO₂ and H₂O-rich fluid inclusions coexisting in the same regions of the samples with distinct modes of homogenization at the same range of temperatures, and V_{CO_2}/V_{FI} variability (Ramboz et al., 1982; Roedder, 1984). Successive phases of fluid evolution are mainly depicted from the trapping of heterogeneous fluid inclusions as a result of partial mixing of magmatic and meteoric fluids in the twophase subsolvus region of the fluid system under variable pressure. Fig. 4a shows three trends of fluid evolution suggesting a combination of processes

Table 2

Equilibrium temperatures a	nd fluid pressures	during hydrothermal	activity in the Cor	reas and Oriente Novo deposits
----------------------------	--------------------	---------------------	---------------------	--------------------------------

Deposit	Styles of mineralization	Rock	Sample	$T_{\rm t}$ (°C)	P_{t} (kbar)
Correas	Qtz-stockwork	Qtz vein	FRT-3a	340-440	2.0-2.6
	Breccia-greisen	Greisen	FRT-1	310-360	1.3-2.0
	Mica-tp-qtz greisen	Greisen	FRT-15	300-340	1.8-2.0
Oriente Novo	Stockwork	Greisen	W-23A	250-300	1.2-1.6
		Qtz vein	W-27A	270-370	1.4-2.4
	Endogreisen	Greisen	AW-28	290-360	1.6-2.1
	Sub-parallel vein	Qtz vein	AW-24G	240-290	1.0-1.5

Abbreviations: Qtz—quartz; tp—topaz; T_t —trapping temperature; P_t —trapping pressure.



Fig. 3. P-T diagrams with representative isochores for the Type I and Type II fluid inclusions from the Correas deposit (A, B, C), and for Type Ia and Ib fluid inclusions from the Oriente Novo deposit (D, E, F, G). The studied rectangular boxes give the P-T conditions of mineralization at each deposit.

involving mixture/immiscibility of three types of fluids, marked by a progressive decrease in trapping temperatures under variable pressure conditions, from 400 to 100 °C. Trend I shows the immiscibility trend of an originally CO₂-rich aqueous carbonic fluid at T~400 $^{\circ}$ C and X_{CO_2} =0.57, which undergoes gas loss caused by hydraulic fracturing and associated pressure fluctuation. This is responsible for the reduction in temperature and important decline of the apparent salinity values related to solute concentrations in the solution, as well as the precipitation of CO₂ dissolved in the aqueous phase (cf. Hedenquist and Henley, 1985; Higgins, 1985a). Trend II represents the dilution of the original fluid by essentially lower T (100–125 $^{\circ}$ C) and lower salinity (3-6 wt.% NaCl eq.) aqueous solutions. The data points within the combined envelopes of the immiscibility and dilution trends may

indicate a combination of the two processes (Hedenquist and Henley, 1985). The dispersion Trend III reflects the isothermal fluid mixing processes (Fig. 4a).

4.4. Stable isotopes

Oxygen and hydrogen isotope analyses were made on quartz, K-feldspar and whole rock in granites, and quartz, topaz, muscovite, zinnwaldite (sense Rieder et al., 1998), cassiterite, and wolframite in quartz-stockwork, breccia greisen and topazite (Table 3). The δ^{18} O for quartz from the breccia greisen and stockwork are remarkably uniform, varying from 10.3‰ to 10.9‰, and indicate a magmatic origin for the fluids (Taylor, 1979; Zhang et al., 1982). They are higher than the values for the topaz–muscovite–albite granite, which range from 6.8‰ to 7.3‰ (Fig. 5). Cassiterite and



Fig. 4. Th (homogenization temperature) vs. salinity (wt.% NaCl eq.) plot for: (a) inclusions in topaz and quartz from Correas deposit; (b) quartz-pods, topaz-mica-quartz bed-like greisen, greisen-stockwork and cassiterite-quartz veins at Santa Bárbara deposit (with isobaric curves from Bodnar et al., 1985); and (c) greisen-pods, greisen veins and quartz veins at Oriente Novo deposit.

wolframite show a narrow range of δ^{18} O, 1.9–3.0‰, much lower than those for coexisting quartz. Zinnwaldite from quartz-stockwork has δ^{18} O in the range of 4.7–5.2‰ and δ D of –67‰ to –86‰, indicating a possible interaction with meteoric water. Muscovite and topaz from topaz-veins have δ^{18} O in the range of 4.7–5.2‰, and δ D varying from –53‰ to –50‰, respectively, denoting isotopic equilibrium during crystallization. These values are very similar to those of quartz and albite-granite, and are consistent with the formation of quartz, topaz and muscovite from the same magmatic fluid. Mica from mica-greisen has very low δ^{18} O of 4.9‰, similar to those of the quartz-stockwork, which also indicates interaction with meteoric fluids. The δ D values of topaz and muscovite range from –44‰ to –65‰, while those of zinnwaldite range from –67‰ to –86‰, and fall in the magmatic water field (Fig. 5).

Selected mineral pairs of quartz, feldspar, wolframite and cassiterite from granite and hydrothermal quartz-veins were chosen, and the temperatures of crystallization were calculated using the isotopic fractionation curves (for quartz-feldspar after Fifarek, 1985; and for quartz-cassiterite-water and quartzwolframite-water after Zhang et al., 1994). The temperatures for coexisting mineral pairs were also utilized for the calculation of the $\delta^{18}O_{H_2O}$ in equilibrium with the mineral associations. Temperatures for cassiterite-quartz equilibrium range from 441 to 459 °C, while those for wolframite-quartz range from 336 to 390 °C. The calculated $\delta^{18}O_{H_2O}$ of the tin-bearing fluids vary from 4.13% to 6.95%, and are consistent with magmatic derived fluids (Taylor, 1979) and the magmatic-hydrothermal fluids of the Sn-W Xihuanshan-China deposit (Zhang et al., 1982).

5. Santa Bárbara deposit (Rondônia tin province)

5.1. Geologic outline

The Santa Bárbara massif is a semicircular stock with a diameter of 7 km and includes three subsolvus granite units (Fig. 6): (1) an early metaluminous porphyritic syenogranite; (2) a peraluminous porphyritic syenogranite; and (3) a central porphyritic albitemicrocline granite (tin-granite). These have been dated by the conventional U–Pb monazite method at 993 ± 5 and 989 ± 13 Ma, and by the SHRIMP U–Pb zircon method at 978 ± 13 Ma, respectively (Sparrenberger, 2003). The tin-granite encompasses two peraluminous granite facies, a pink medium-grained porphyritic albite-microcline granite and a pink to white fine-

Table 3

Summary of oxygen and hydrogen-isotope composition of granite types and mineral phases from the Correas, Santa Bárbara and Oriente Novo deposits

Deposit	Stage	Rock or	Sample	δD SMOW	V (‰)			$\delta^{18}C$	SMOW	(‰)					
		Facies		WR	Kfs	Mica	Kln	WR	Qtz	Тр	Kfs	Mica	Cas	Wolf	f Tp
Correas	Magmatic	Bt granite I	A-20	-68				7.8	10.3		7.0				
		Bt granite II	A-21	*-82/-78				9.7	9.6		9.3				
		Bt-ms granite	A-22	-91		-89		4.9	*-9.9/		3.2	5.1			
									-9.6						
		Ab granite I	A-23	-65				7.5	7.3						
		Ab granite II	A-24	-87				6.4	6.8						
	Post-Magmatic	Mica-tp-qtz	A-11								10.5				
		greisen	A-12								9.9				
		Breccia-greisen	A-13								*10.9/				
											10.6				
			A-14								10.3				
			A-15								10.5			1.9	
			A-16								*10.6/		2.8	2.8	
		a i i i									10.3				
		Qtz stockwork	A-17				-86				10.6		2.7	,	
			A-18				-67				10.5		*2.7/		
													2.4/		
			A 10								10.7		4.7		
		T	A-19				(5			4.4	10.7	7.2	3.0		7 2
		Topazitic veins	A-07				-05			-44		/.3	3.4		7.5
		Miss maison	A-08				-33	/		-50		8.4	2.7		1.5
		(and agraisan)	A-10				51					4.9			
Santa Bárbara	Magmatic	Syenogranite	AM-52B		-98	-118	-51	7.3	9.4		6.9	1.5			
Daroara		Svenogranite	AM-53		_74	-110			10.3		9.0	5.8			
		Ab-mc granite	AM-108		/ 4	-92			10.5		2.0	67			
		Ab-mc granite	AM-145		-123	-93		87	93		78	4.8			
		White ab	AM-134		120	-125		0.17	11.3		/10	7.9			
		granite													
		Pegmatite	AM-213		-68	-106			10.0		4.5	7.3			
	Late-Magmatic	Quartz pod	AM-168			-124			9.8			7.9			7.5
	e	Salmon ab	AM-14a		-67	-127			9.8		*1.7/1.5	5.2			
		granite													
		Bedded	AM-35			-99			10.0			*1.4/	2.9		
		greisen										2.0			
	Post-Magmatic	Greisen vein	AM-130			-124			11.8			4.7			
		Greisen vein	AM-174c			-133			11.7			5.9			
		Qtz-cas vein	AM-131						11.7				3.5		
		Greisen vein	AM-297			-102			9.7			*2.1/			
												1.8			
		Barren qtz	AM-159a						*0.7/0.6						
		vein													
		Mica greisen	AM-74c			-102						*-0.8/			
		vein										-0.3			
		Ms vein	AM-307									*-6.2/	3.3		
		Kln vein	AM-298	-69				15.7				-6.1			

(continued on next page)

Deposit	Stage	Rock or	Sample	$\delta D SMO$	W (‰)			$\delta^{18}C$	SMOW	V (‰)				
		Facies		WR	Kfs	Mica	Kln	WR	Qtz	Тр	Kfs	Mica	Cas	Wolf Tp
Oriente Novo	Post-Magmatic	Li-mica alkali-feldspar granite	3524A			-92						6.4		
		Stockwork	W-23A			-101						6.3		
		Endogreisen	AW-8b			-91						6.6		
		Sub-parallel sheeted-veins	W-12b			-112						6.4		

Table 3 (continued)

Abbreviations: *--duplicate analysis. Bt---biotite; Cas---cassiterite; Kln---kaolinite; Kfs--K-feldspar; Ms---muscovite; Qtz---quartz; Tp----topaz; Wolf----wolframite; WR---whole rock.

grained equigranular to porphyritic albite-microcline granite; the latter occupies the apical part of the cupola. The main minerals are quartz, albite, microcline, and zinnwaldite; accessory minerals comprise fluorite, topaz, zircon, thorite, columbite, cerianite, and cassiterite. Pegmatoid pods (up to 2 m in diameter) and snowball, granophyric, and unidirectional solidification textures are common (Fig. 4). The tin granites are of magmatic origin, and they were affected by subsolidus reactions and hydrothermal alteration represented by greisenization, albitization, silicification,



Fig. 5. δD vs. $\delta^{18}O$ diagram showing the calculated $\delta^{18}O$ and δD values for stockwork/veins and greisens from the Correas deposit. Abbreviations: Bt—biotite; Ab—albite; qtz—quartz; tp—topaz; ms—muscovite; wr—whole rock.

muscovitization, and argillization during late magmatic-hydrothermal and post-magmatic stages (Sparrenberger, 2003).

These granites are characterized by high SiO₂, K_2O , Na_2O , $Fe_2O_3/(Fe_2O_3+MgO)$, Sn, Rb, Ce, Nb, Ga, Y, F, Li, U and Th contents, and low concentrations of CaO, MgO, TiO₂, Al₂O₃, Ba, Sr and Zr. They also show high total REE contents, are slightly enriched in LREE, and exhibit a strong negative Eu anomaly. The white albite-microcline granite shows more evolved patterns characterized by higher Ga, Li, Ta, Y, and total REE, than the other tin-specialized granites (Sparrenberger, 2003).

5.2. Mineralization

The Santa Bárbara deposit covers an area of ~500 m by 150 m. The tin deposit encompasses two styles of mineralization (Fig. 6): (1) bed-like cassiterite-bearing topaz-zinnwaldite-quartz greisen bodies, up to 40 m thick, and salmon colored albitized granites (Taboquinha greisen); and (2) a vein-veinlet/stockwork, encompassing brittle fracture zones containing topazzinnwaldite-quartz greisen veins with cassiterite-wolframite, quartz-cassiterite veins, muscovite veins, and late kaolinite stockwork/veinlets (Sparrenberger, 2003). The mineral paragenesis is shown in Fig. 7.

5.3. Fluid inclusions

The fluid inclusions study was performed on topaz and quartz from the white albite-microcline granite, pegmatite, quartz pod, bedded greisen, salmon albitized granite, greisen stockwork, and quartz veins (Table 4). Microthermometric studies



Fig. 6. Geological map of the Santa Bárbara massif showing the granitic facies, limits of the Santa Bárbara tin deposit (modified after Frank, 1990; Payolla et al., 2002), and styles of mineralization. Abbreviations: tp—topaz; qtz—quartz; USTs—unidirectional solidification textures. Inset in upper panel shows location relative to Brazil.



Fig. 7. Simplified paragenetic and mineral formation stages at the Santa Bárbara deposit.

were carried out on unmodified primary fluid inclusions with irregular or negative crystal morphology. Secondary inclusions located along trails were also studied. The fluid inclusions were classified as follows: Type I primary melt inclusions are abundant in topaz from bedded greisens and greisen stockwork, and in topaz and/or quartz in the white albite granite and salmon albitized granite. They contain a Na-rich aqueous phase and vapor or gas phases and have salinities in the range 10-15 wt.% NaCl eq. A few solid phases of melt inclusion in topaz from bedded greisen were analyzed via micro-Raman, and are represented by topaz and quartz. Type II composite fluid inclusions are found in quartz and topaz from white albite granite and greisen stockwork and constitute accidentally trapped solid minerals together with minor proportions of vapor/ gas or liquid. Type III (H₂O-NaCl±KCl±CaCl₂±

FeCl₂) aqueous fluid inclusions are associated with topaz and quartz in all analyzed samples, and range from monophase to multiphase. The primary inclusions comprise 5-90 vol.% of vapor, salinities in the range of 0.3-42 wt.% NaCl eq., with predominance of values between 5 and 14 wt.% NaCl eq., and homogenize into the liquid or the vapor phase at 89-506 °C. Some of these fluid inclusions could be considered as high saline brine inclusions, similar to those described by Roedder (1984). Type IV aqueous fluid (H₂O–NaCl±KCl) inclusions are observed only in quartz from the quartz-cassiterite vein. Their salinities vary between 0.3 and 7.0 wt.% NaCl eq., but predominate in the 0-3 wt.% NaCl eq. range. The volumetric proportion of the vapor bubble varies from 10 to 90 vol.%, and homogenization into the liquid or vapor phase occurs between 153 and 375 °C, but predominantly at 320–380 °C; Type V

Table 4							
Summary	of flu	id inclusior	data	from	Santa	Bárbara	deposit

Stage	Granites and morpho-structural types	Mineral	Type of fluid inclusion	Tm_{CO_2} (°C)	<i>T</i> _c (°C)	Th _{CO2} (°C)	Salinity (wt.% NaCl eq.)	Th (°C)	Fluid behaviour T_t (°C)
Magmatic	White Albite–Microcline Granite	Qtz+Tp	Type I Type III Type V (H ₂ O±CO ₂ ±CH ₄)	-58.2 to -56.8	$\begin{array}{l} Qz \ (p_1) - 50 \ to -22 \\ Qz \ (p_2) - 54 \ to -44 \\ Qz \ (p_3) - 42.3 \\ Qz \ (s) -40 \ to -21 \\ Tp \ (s) -42 \ to -25 \\ (Na\pm Ca\pm Fe\pm K) \end{array}$	10.9	$\begin{array}{c} Qz \ (p_1) \ 5 \ to \ 12 \\ Qz \ (p_2) \ 14 \ to \ 42 \\ Qz \ (p_3) \ 34 \\ Qz \ (s) \ 0 \ to \ 3 \\ Tp \ (s) \ 3 \ to \ 19 \end{array}$	(I)>600 Qz (p ₁) 123-452 (III, V) Qz (p ₂) 90-216 (III) Qz(p ₃) 330 (III) Qz (s) 164-380 (III) Tp (s) 356-553 (<390) (III,V)	Immiscibility T _t (s)=350–370
	Pegmatite	Qtz	Type III Type V (H ₂ O±CO ₂ ±CH ₄)	_	(s) -40 to -28 (Na±Ca±Fe±K)	_	(s) 0 to 6	(s ₁) 327–370 (s ₂) 114–302 (>230) (III) 128–304 (240–250) (V)	Immiscibility in secondary inclusions $T_t(s)=350-370$
Magmatic-hydrothermal	Quartz–Pods	Qtz+Tp	Type III Type V	-58.6 to -57.8	Qz (p) -49 to -24 Qz (s) -50 to -21 Tp (p, ps) -51 to -23	15.9 to 30.3	Qz (p) 4 to 21 Qz (s) 6 to 17	Qz (p) 97–417 (100–140) (III) Qz (p) 206–524 (V)	
			(H ₂ O±CO ₂ ±CH ₄)		Tp (s) -47 to -25 (Na \pm Ca \pm Fe \pm K)		Tp (p, ps) 7 to 15 Tp (s) 10 to 23	Tp (p) 400–500 (450–490) (III) Qz (s) 100–410 (III, V)	Immiscibility ($T_t(p)=500-510$); Fluid mixing
								Tp (s) 446–484 (460–470) (III) Tp (ps) 375–573 (400–490) (V)	
	Bedded–Greisen	Qtz+Tp	Type I Type III Type V (H ₂ O±CO ₂ ±CH ₄)	-57.5 to -56.7	$\begin{array}{l} Qz \ (p) \ -41 \ to \ -28 \\ Qz \ (ps) \ -54 \ to \ -28 \\ Qz \ (s_1) \ -53 \ to \ -23 \\ Qz \ (s_2) \ -36 \end{array}$	_	$\begin{array}{l} Qz \; (p) \; 3 \; to \; 9 \\ Qz \; (ps) \; 1 \; to \; 13 \\ Qz \; (s_1) \; 0 \; to \; 22 \\ Qz \; (s_2) \; 0 \; to \; 2 \end{array}$	(I)>600 Qz (p) 355–379 (V) Tp (p) 211–353 (III) Tp (p) 337–424 (340–370) (V)	Immiscibility ($T_1(p)=350-370$); Fluid mixing
					Tp (p) -43 to -24 (Na+Ca+Fe+K)		Tp (p) 2 to 14	Qz (ps) 127–424 (330–370) (III) Oz (s) 102–332	
	Salmon Albitized Granite	Qtz	Type I Type III (H ₂ O+CO ₂ -traces)	-	(p, ps) -47 to -31 (Na \pm Ca \pm Fe \pm K)	-	(I) 9 to 12 (p, ps) 1 to 8	(I) >600 (p, ps) 150-404	Immiscibility (T_t (p)=350–370); Fluid mixing (final stages)
Post-magmatic	Greisen–Vein (Stockwork)	Qtz+Tp	Type III Type V	-57.8 to-56.6	Qz (p) -52 to -11 Qz (s) -48 to -28	16.7 to 19.8	Qz (p) 2 to 18 Qz (s) 0 to 6	Qz (p) 78–435 (>320) (III) Tp (p) 272–446 (III, V)	Immiscibility ($T_t(p)=350-370$); Elicid activity ($T_t(p)=350-370$);
			$(H_2O\pm CO_2\pm CH_4)$		Tp (p) -48 to -32 (Na±Ca±Fe±K)		Tp (p) 1 to 22	Qz (s) 124–415 (III)	Fiuld mixing (final stages)
	Cassiterite-Quartz-Vein	Qtz	Type III Type IV H ₂ O	_	(p) -31 to -26 (Na±K) (s) -48 to -28	_	(p) 0 to 7 (s) 2 to 15	(p) 153–375 (320–380) (IV) (s) 110–177 (III)	Boiling ($T_t(p)=350-370$); Evolution to $\langle T_t \rangle$ salinity fluids
	Late Quartz–Vein (barren)	Qtz	Type III H ₂ O	_	$(Na\pm Ca\pm Fe\pm K)$ $(p) -42 \text{ to } -34$ $(Na\pm Ca\pm Fe\pm K)$ $(s) -58 \text{ to } -47$ $(Na\pm Ca\pm K)$	_	(p) 1 to 6 (s) 15 to 19	(p) 145–415 (s) 94–147	Boiling involving meteoric fluids; Evolution to $\langle T_r \rangle$ salinity fluids

Abbreviations: Qtz-quartz; Tp-topaz; p-primary inclusions; s-secondary inclusions; ps-pseudosecondary inclusions; Tm_{CO2} -CO₂ melting temperature; T_e -eutectic temperature; Th_{CO2} -CO₂ homogenization temperature; T_t -trapping temperature.

 $(H_2O-CO_2\pm CH_4-NaCl\pm KCl\pm CaCl_2\pm FeCl_2)$ primary aqueous-carbonic fluid inclusions are found in topaz from the white albite granite, quartz pod, bedded greisen and greisen stockwork. They are biphase (H₂Ol-CO₂ g), rarely triphase (H₂Ol-CO₂l- CO_2 g) or multiphase (H₂Ol±CO₂l-CO₂ g-solid phases). The proportion of the CO₂ phase varies between 25 and 90 vol.%. The salinities vary in the range of 2-25 wt.% NaCl eq., but predominantly between 5 and 12 wt.% NaCl eq. Th into the CO₂ or H₂O phases occurs between 128 and 553 °C, mainly in the 340-390 °C range. They also have varying concentrations of CH₄, and include very high X_{H₂O}, and high X_{H₂O} fluid inclusion sub-types (cf. Diamond, 1994, 2001). Secondary inclusions, related to meteoric fluids, are aqueous and have low salinity (0-3 wt.% NaCl eq.) and Th (94-380 °C). Proportion of the vapor phase is between 10 and 55 vol.% and the composition is similar to Type III inclusions.

The CO₂- and H₂O-rich inclusions have the immiscibility characteristics cited by Ramboz et al. (1982). Their trapping temperatures were obtained from several diagrams of the type homogenization temperature vs. the ratio of gas or vapor volume to total volume (Th $\times V_{v/g}/V_{FI}$), because the low molar fraction of CO₂ precluded measurement of the homogenization temperature of the phase and thus of the isochore calculations. The white albitemicrocline granite (Table 4) shows primary meltinclusions, primary aqueous and aqueous-carbonic fluid inclusions in re-equilibrated quartz, and secondary aqueous-carbonic inclusions in topaz, at trapping temperatures of 350-370 °C. The early evolution of the pervasive late magmatic hydrothermal fluid started at ~510 °C, and is represented by the quartz pods. Primary and pseudo-secondary aqueous inclusions observed in topaz from these pods are rich in calcite crystals and are thought to provide evidence for CO₂ degassing and of immiscibility near the critical point of the system. These processes would cause extensive calcite precipitation and diminution of CO₂ contents in the fluid. At a later stage, the system evolved into immiscible solutions trapped at lower temperatures (350-370 °C) represented by the primary fluid inclusions in bedded-greisens (magmatic-hydrothermal stage), affected by fluid mixture with meteoric hydrothermal fluids; the latter are represented by low salinity secondary fluid inclusions, at even lower temperatures (Table 4). Post-magmatic fluids related to fissural alteration were trapped at similar temperatures with minor meteoric hydrothermal fluid influx, and are recorded within the greisen stockwork and quartz-cassiterite vein systems (Table 5). It is worth noting that the inclusions present in quartz-cassiterite veins are the only representatives of Type IV, and reflect particular conditions of cassiterite deposition. Almost pure meteoric hydrothermal fluids were trapped in late barren quartzveins at temperatures as low as 145 °C. High salinity Ca-rich fluids, trapped at temperatures of 120-90 °C, were also observed in many samples (Table 4), and seem to reflect decrease of temperatures and correspondent increase of salinities and Ca content in the solutions.

The temperature vs. salinity diagram (Fig. 4b) shows a fluid evolution model for the quartz pods, bedded-greisen, greisen stockwork, and quartz-cassiterite veins. It comprises three trends, suggesting a combination of distinct progressive immiscibility, degassing and dilution processes (Hedenquist and Henley, 1985; Wilkinson, 2001). These are marked by decrease in trapping temperatures under variable pressure conditions: Trend I represents the immiscibility trend of an originally aqueous-carbonic fluid associated with CO₂ degassing near the critical point of the system, at T=500 °C and $P\sim500$ bar; Trend II shows the immiscibility trend of an originally CO₂ poor aqueous-carbonic fluid with very low X_{CO₂} (not measurable), accompanied by gas loss at T=350-370 °C and $P\sim200$ bar; and Trend III shows the effect of dilution of the original fluid by less saline, cooler water from 350 to 370 °C to 130 °C at ~10 bar.

5.4. Stable isotopes

Isotope analyses were made on K-feldspar, quartz and mica from granites and pegmatite, and quartz, mica, topaz, kaolinite, and muscovite, separated from the quartz pods, bedded-greisens, salmon albitized granites, greisen stockwork, quartz–cassiterite and muscovite veins, and kaolinite stockwork (Table 3). We determined equilibrium temperatures of quartz– feldspar, quartz–topaz and quartz–cassiterite pairs, utilizing the fractionation quartz–topaz and quartz–

	•			6	í í	í (E			:	1007
	Styles of mineralization	Rock/Sample	Mineral	Type of fluid	Tm _{CO2} (°C)	T_{e} (°C)	Tm _{clathrate}	Th _{CO2} (°C)	$d_{\mathrm{CO}_2}^{\mathrm{d}}$	Salinity (wt.% NaCl eq.)	Th _{aq} /Th _{total} (°C)
				Inclusion							
Post-magmatic				Ia	-57.9 to -56.8	-28.8 to -23.0	1.5 - 8.2	25.6-29.9	0.26-0.70	3.6-13.8	190-440
	Stockwork		Qtz Tp	ll	-57.7 to -57.0	Ι	2.9 - 6.4	24.9 - 30.6	0.24 - 0.68	6.8-12.1	210 - 360
		HC2-W		Π	I	-29.9 to -22.9	1.9 - 6.0	I	Ι	7.4–13.3	155–335
		,		Ia	-57.8 to -56.6	27.6 to -23.3	4.1 - 8.6	12.0 - 26.7	0.68 - 0.85	2.8 - 10.4	190 - 410
	Stockwork		Qtz	lb	-57.8 to -56.8	Ι	I	16.4 - 28.8	0.17 - 0.81	I	240 - 370
		W-2/A		Π	I	-27.6 to -25.6	7.5 - 8.0	I	I	4.0 - 4.9	120-320
				Ia	-59.0 to -57.1	-27.8 to -23.2	5.3 - 9.8	14.5 - 25.8	0.21 - 0.83	0.4 - 8.6	210-420
	Endogreisen	Ureisen pou/	Qtz Tp	lb	-59.1 to -57.3	I	8.4–9.1	10.8 - 25.9	0.14 - 0.86	1.8 - 3.2	245 - 380
		07-MW		II	I	-27.0 to -25.3	5.4 - 8.9		I	2.4-8.4	100 - 305
				Ia	-57.3 to -56.6	-27.6 to -27.0	4.4-7.9	26.0 - 30.2	0.26 - 0.66	4.1 - 9.9	190-405
	Sub-parallel vein		Qtz	lb	-57.8 to -57.0	I	I	26.1 - 29.3	0.26 - 0.69	I	220-320
		D+7-W		II	I	-29.8 to -26.8	4.4-8.2		Ι	3.6 - 9.9	140 - 290
Abbreviations: Tm _{CO2} —CO2	Qtz—quartz; Tp—t melting temperature;	ppaz; Ia—aqueot T_{e} —eutectic ter	us-carbonic mperature;	c fluid (H ₂ (Tm _{clathrate}	O-CO ₂ -CH ₄ -NaCl —temperature of d); Ib—aqueous-car lisassociation of a	rbonic fluid (gas clathrat	(CO ₂ -H ₂ O-C e; Th _{CO2} -CO	H ₄ –NaCl); II D ₂ homogeni		tter-rich fluid $d_{\rm CO_2}$ —CO ₂

Table 5

feldspar curves of Zheng (1993a,b), and quartzcassiterite curves of Zhang et al. (1994). The δ^{18} O and δD of the coexisting hydrothermal fluids in equilibrium with these minerals were calculated by using the quartz-water curve of Matsuhisa et al. (1979), the feldspar-water curves of O'Neil and Taylor (1967), Bottinga and Javoy (1973) and Zheng (1993a), the biotite-water curve of Zheng (1993b), topaz-water curve of Zheng (1993a), cassiteritewater curve of Zhang et al. (1994), kaolinite-water curves of Sheppard and Gilg (1996) and Gilg and Sheppard (1996), muscovite-water curve of Zheng (1993b), and the calculated curve of Jenkin (1998) for micas. All the oxygen and hydrogen data are shown in Table 3. Oxygen isotope geothermometry indicates that the minimal retrograde reaction temperature for a quartz-feldspar pair is in the order of 603 °C, for the syenogranites. Formation of the quartz pods and bed-like greisen bodies took place at ~570 and 500 °C, respectively, and that of the cassiterite-quartz veins at 415 °C. These temperatures are 45-130 °C higher than the fluid inclusion trapping temperatures.

The calculated $\delta^{18}O_{H_2O}$ of the tin-bearing fluids in equilibrium with host metasomatites ($\delta^{18}O_{H_2O}=5.2-7.3\%$; quartz–water pair) indicates that the fluids equilibrated with an evolving residual granitic magma or with a high temperature albite-granite, consistent with a magmatic origin (cf. Sheppard, 1986). The calculated $\delta^{18}O_{H_2O}$ deduced from the equilibrium mica-water indicates mixture with meteoric water, already at the pervasive magmatic-hydrothermal stage ($\delta^{18}O_{H_2O}=1.1-9.8\%$). The late muscovite veins ($\delta^{18}O_{H_2O}=-6.4\%$ at 380 °C) and late quartz ($\delta^{18}O_{H_2O}=-3.8\%$ at 380 °C) formed at the postmagmatic fissural hydrothermal alteration stage, implying a dominant meteoric water component (Fig. 8).

Measured δ^{18} O and δ D and the data for mineralizing fluids in equilibrium with kaolinite at 100 °C are also shown in Table 3. The data plot near the magmatic water field, and the fluid is enriched in heavy hydrogen compared with the host granites (Fig. 8). Also some data points for the greisen seem to plot along a tie line leading to the composition of the kaolinite veins. This might suggest a mica-clay mixing line, resulting from a dominant magmatic fluid mixed with meteoric water, or deuterium enrich-



Fig. 8. δD vs. $\delta^{18}O$ diagram showing the fluid isotopic composition of the Santa Bárbara deposit, based on calculated δD_{H_2O} and $\delta^{18}O_{H_2O}$ values. Abbreviations: Ab—albite; mc—microcline; gr—granite. AM-52B, AM-53, AM-108 and AM-145 denote sample numbers.

ment of the waters caused by deuterium modifying processes.

6. Oriente Novo deposit (Rondônia Tin Province)

6.1. Geologic outline

The Oriente Novo massif occupies approximately 80 km², is subcircular in shape and intrudes Proterozoic (1.75-1.43 Ga) basement rocks and the Santa Clara batholith (Fig. 9). The massif consists of a central porphyritic biotite (±hornblende) monzogranites surrounded by a medium-grained porphyritic biotite syenogranite. Fine-grained porphyritic biotite syenogranite and muscovite-biotite microsyenogranite are found along the western border of the massif. Small late-stage bodies of siderophyllite-alkali-feldspar granite, alaskite, biotite (±alkali amphibole) microgranite, zinnwaldite-alkali-feldspar granite, and rhyolite porphyry are found in the west-central part. Alkali feldspar microsyenite, trachyte, trachyandesite, microgranite and, more rarely, aplite and pegmatite occur as dykes within and/or close to the massif. The primary rare-metal (Sn, Ta, Nb, W) deposits are associated with siderophyllite-alkali-feldspar granite and alaskite, as well as with zinnwaldite-alkali feldspar granite and rhyolite porphyry (Leite, 2002). The siderophyllitealkali feldspar granite and alaskite are composed of orthoclase perthite and microcline, round and irregular quartz, albite-oligoclase, and siderophyllite. Zircon, monazite and ilmenite are the primary accessory

minerals. The zinnwaldite-alkali feldspar granite and rhyolite porphyry show porphyritic texture, and exhibit poikilitic microcline and quartz megacrystals (<0.5 cm) dispersed in an albite-dominated fine- to very fine-grained matrix. The megacrystals include albite laths sometimes with a snowball texture. Zinnwaldite is present and includes zircon, fluorite, rutile, cassiterite, and columbite-tantalite crystals. The siderophyllite-alkali feldspar granite and alaskite are high in SiO₂, F, Rb, U, Y, and low in TiO₂, Al₂O₃, Fe₂O₃ total, MgO, CaO, P₂O₅, Ba, Sr, and Eu, whereas the zinnwaldite-alkali feldspar granite and rhyolite porphyry are low in SiO₂, TiO₂, Fe₂O₃ total, CaO, K₂O, and high in Al₂O₃, Na₂O, Li, Rb, Ga, Nb, Sn, and Ta (Leite, 2002). These geochemical characteristics are similar to those of rare-metal peraluminous granites (see, e.g., Pollard, 1989a).

6.2. Mineralization

The primary deposit occupies an area of $\sim 1.5 \text{ km}^2$ in the west-central part of the Oriente Novo massif. Major styles of mineralization can be divided into three groups (Fig. 9): (1) stockwork of veins/veinlets of greisen with cassiterite and of quartz with cassiterite and wolframite hosted by older mediumgrained porphyritic biotite syenogranite; (2) disseminated cassiterite and columbite–tantalite in the zinnwaldite alkali feldspar granite with cassiterite-bearing greisen pods; and (3) sub-parallel veins/veinlets of greisen with cassiterite and of quartz with cassiterite and wolframite having a general strike of N30–50° E



Fig. 9. Schematic geological map of the Oriente Novo massif showing the granitic facies, and the styles of mineralization of the Oriente Novo deposit (modified after Leite, 2002). Abbreviations: Bt—biotite; alk—alkali. Inset shows location relative to Brazil.

and a dip of 50–80° SE. The stockwork mineralization is interpreted to be genetically related to the siderophyllite-alkali feldspar granite and alaskite, whereas the disseminated, endogreisen and sub-parallel vein/ veinlet mineralization systems are related to the zinnwaldite-alkali feldspar granite and rhyolite porphyry (Leite, 2002). The mineral paragenesis is illustrated in Fig. 2.

6.3. Fluid inclusions

Fluid inclusions have been studied in samples of greisen pods and veins, and quartz veins. Two types of primary fluid inclusion are found in topaz and quartz at room temperature (Table 5). Type I aqueous carbonic fluid inclusions ($H_2O\pm CO_2-CH_4$ -NaCl) are the most abundant. Two subtypes are distin-

guished based on the volumetric proportion of the CO₂ phase: subtype Ia (10%<CO₂<70%) and subtype Ib ($CO_2 > 80\%$). They show low to moderate salinity (0.4-13.8 wt.% NaCl eq.) and the total homogenization, into the H₂O or CO₂ phases, takes place at temperatures varying from 190 to 440 °C, with peaks at 240-290, 280-330, and 310-360 °C. Type II fluid inclusions contain small amounts of CO₂ in addition to the water-rich fluid (H₂O–CO₂–NaCl). The CO₂ was detected by melting clathrate temperatures during heating experiments. The type II inclusions have low to moderate salinities (2.4-14.1 wt.% NaCl eq.) very similar to type I, but show lower homogenization temperatures (100-340 °C), with peaks at 200-250 and 250-300 °C. Trapping conditions of Type Ia and Ib immiscible fluids, obtained from intersection of isochores, took place between 240 and 370 °C and 1.0–2.4 kbar (Table 2; Fig. 3D through G). The type I and II inclusions (those with Th>240 °C) have resulted from effervescence of a similar aqueouscarbonic fluid derived from a late-magmatic parental fluid phase. This was genetically related to the siderophyllite-alkali feldspar granite and alaskite and to the zinnwaldite-alkali feldspar granite and rhyolite porphyry. Type II (Th<240 °C) inclusions are probably products of a mixture of a magmatic CO₂bearing water-rich fluid and some meteoric water in all styles of mineralization. The fluid evolution is similar to that of the Correas deposit (Fig. 4a,c).

6.4. Stable isotopes

Oxygen and hydrogen isotope composition was determined for zinnwaldite from alkali-feldspar granite, greisen pod, greisen vein (stockwork), and subparallel quartz vein (Table 3). A formation temperature of 300 °C for Li-mica in greisen and quartz veins was calculated using the average temperature of total homogenization of fluid inclusions in cogenetic topaz and/or quartz. For the zinnwaldite from the alkali feldspar granite, we applied the estimated temperature of 650 °C of Manning (1982), which is the minimum experimental crystallization temperature for F-rich granites at pressure of 1 kbar. The $\delta^{18}O_{H_2O}$ in equilibrium with the zinnwaldites was calculated using the biotite-water fractionation curve of Zheng (1993b). The $\delta D_{H_2}O$ in equilibrium with zinnwaldite from alkali-feldspar granite was calculated using the



Fig. 10. δD vs. $\delta^{18}O$ diagram showing the calculated $\delta^{18}O$ and δD for Li-mica alkali feldspar granite and greisens from Oriente Novo deposit. Abbreviations indicate sample numbers.

mica-water fractionation curve of Suzuoki and Epstein (1976). The water in equilibrium with zinnwaldite from alkali-feldspar granite ($\delta^{18}O_{H,O}$ =8.9%; $\delta D_{H,O}$ = -6.9%) overlaps the field of the typical magmatic water (Fig. 10). The calculated $\delta^{18}O_{H,O}$ values of fluids in equilibrium with zinnwaldite from greisen (7.4‰ and 7.7‰) and quartz vein (7.5‰) also overlap with the field of magmatic water. The calculated δD values for the zinnwaldites from greisen (-66% and -76%) and quartz vein (-87%) are low enough to suggest a meteoric component in the hydrothermal fluids responsible for the formation of greisen and quartz vein (Fig. 10). However, this may also reflect outgassing of earlier fluids from the magma (Taylor, 1986), depletion of late-magmatic fluids in deuterium (Carten et al., 1988), or variations linked to fluidmagma isotope effects (Rye et al., 1990).

7. Discussion

The geological, petrographic, fluid inclusion, and stable-isotope studies point to a number of common and contrasting features of the studied Sn-polymetallic greisen-type deposits. The tin-granites of the Itu Rapakivi Province are related to the post-collisional stage of the Brasiliano orogeny (625 ± 5 Ma) (Wernick et al., 1997; Campos Neto, 2000), whereas those of the Rondônia Tin Province are considered anorogenic like the Younger Granites of Nigeria (Kloosterman, 1970; Priem et al., 1989). More recently, however, the tin-granites and related rocks of the Rondônia Tin Province were interpreted as inboard rapakivi magmatism temporally related to the Rondonian-San Ignacio (1.50–1.30 Ga) and Sunsás (1.25–1.00 Ga) orogenies (Bettencourt et al., 1999). In both provinces, the tin-granites are fluorine-rich peraluminous alkali feldspar granites and contain topaz and/or muscovite or zinnwaldite; the porphyritic facies shows "snowball" texture, indicative of magmatic origin (Pollard, 1989b; Sun and Yu, 1992). Their geochemical characteristics are comparable to the low P_2O_5 (<0.10 wt.%) sub-type of topaz-bearing granites (Taylor, 1992). A meta-igneous source for these granites is considered possible.

The Santa Bárbara and Oriente Novo deposits occur within granites, whereas the Correas deposit is hosted in gneisses and calc-silicate rocks. An important point is the common occurrence of stockworks and veins at Correas and Oriente Novo deposits. In contrast, the Santa Bárbara deposit is dominantly a preserved mineralized cupola with associated bed-like greisen bodies. These deposits contain a similar raremetal suite that includes Sn (\pm W, \pm Ta, \pm Nb), but Zn–Cu–Pb mineralization is present only in Correas deposit.

High temperature fluid inclusions were identified only at the Santa Bárbara deposit. They are represented by primary silicate-melt inclusions with a Narich aqueous-phase, with or without CO_2 , and salinity from 0.5 to 15 wt.% NaCl eq. They indicate a minimum crystallization temperature for the albite granite at Tt \geq 600 °C.

The early primary fluids related to mineralization in the Correas and Oriente Novo deposits have common features: they are low-salinity (0–19 wt.% NaCl eq.) CO_2 -bearing aqueous fluids, which homogenize between 245 and 450 °C. In the Santa Bárbara deposit, this early fluid is represented by low-salinity (5–12 wt.% NaCl eq.), low CO_2 -bearing aqueous fluids, which homogenize at a more restricted temperature range (340–390 °C). In the Santa Bárbara, Oriente Novo and Correas deposits, this type of fluid may account for the deposition of early-disseminated cassiterite and columbite–tantalite, either directly from a melt or from a coexisting vapor, as well as from a late-magmatic fluid (see Haapala, 1997; Linnen, 1998). The compositional range and homogenization behavior in the Santa Bárbara and Oriente Novo deposits is consistent with immiscibility around 350– 370 °C and 350–450 °C, respectively. This process is responsible for the successive precipitation of cassiterite, wolframite and minor columbite–tantalite, down to the temperature of ~250 °C. These oxides continued to grow up to the post-magmatic stage in the presence of a magmatic-derived fluid mixed with external fluids. The occurrence of scheelite in the Santa Bárbara deposit is better explained by remobilization of tungsten and its subsequent deposition as scheelite in the late-magmatic stage.

The second type of fluid inclusions, also related to deposition of cassiterite, wolframite and minor columbite–tantalite (inclusions in cassiterite) in Oriente Novo deposit (Th>240 °C) and sulfide in Correas deposit, is essentially represented by aqueous solutions with minor CO₂ and low to moderate-salinities (0–14.1 wt.% NaCl eq.), which homogenize between 100 and 340 °C. In the Santa Bárbara deposit these fluids are represented by aqueous fluid inclusions in quartz–cassiterite veins, which have low salinities (0.3–3.0 wt.% NaCl eq.) and homogenize at 320–380 °C.

The trapping P-T conditions (P_t, T_t) of the observed early fluids in the Correas and Oriente Novo deposits, obtained from fluid-inclusions, suggest hydrothermal activity at 240-440 °C and 1.0-2.6 kbar, close to lithostatic. The observed progressive decrease in T_t and P_t indicate either erosion of overlying rock or an open hydrostatic system and hydraulic fracturing of the host-rocks. The contrasting fact is that in the Santa Bárbara deposit, the early magmatic and late post-magmatic fluids indicate similar T_t from 350 to 400 °C and a P_t from 300 to 200 bar, near hydrostatic. The depth of emplacement at Oriente Novo and Correas deposit is roughly the same (maximum=9.8 km) and is compatible with a transitional hypabyssal to plutonic environment. The Santa Bárbara deposit is more shallow (maximum=1.8 km), characteristic of subvolcanic environment. These fluids affected the magmatic-stage rocks and modified the primary fluid inclusions of quartz from granites, attesting some hydro-fracturing and mineral equilibrium at the post-magmatic stage.

The late post-magmatic fluid observed in Correas deposit was a CO_2 -free aqueous solution, with low salinity (0–6 wt.% NaCl eq.), and a homogenization temperature between 100 and 260 °C. It characterizes

the sulfide–fluorite–sericite Correas deposit association. In the Santa Bárbara deposit, later-stage postmagmatic aqueous fluids show a much larger range of homogenization temperatures (94–380 °C) than in the other deposits, lower salinity (0–3 wt.% NaCl eq.), and include late-barren-quartz, muscovite, and kaolinite veins. The low temperature (120–90 °C) late fluid type at the Santa Bárbara deposit is also high-saline Ca-rich, and was associated with meteoric hydrothermal water that percolated along fissures (open system) at shallow depths. A cold low-salinity fluid and neutralization of acid condensates from the previous acid fluids are responsible for the kaolinite veins.

In all cases the post-magmatic late fluids resulted from decreasing temperature as mixing and dilution proceeded below 290 °C. The switch-over of the process would lead to the predominance of an essentially aqueous solution (H_2O –NaCl±KCl) system. These fluids may represent a mixture of magmatic derived fluids and hydrothermal meteoric water (dominant) components, or different overprints on granites of diverse chemical composition.

The oxygen and hydrogen stable isotope data indicate that the fluids contained a magmatic component mixed with meteoric water. Hydrofracturing, immiscibility, greisenization and loss of CO_2 ($\pm CH_4$) with falling temperature, are the principal processes responsible for Sn-W deposition. In the Santa Bárbara deposit, oxygen isotope geothermometry indicates temperatures of 500 °C for the bed-like greisen bodies, and 400 °C for the cassiterite-quartz veins. The calculated isotopic composition of water in equilibrium with host metasomatites ($\delta^{18}O_{H_2O}=1.1-$ 9.8‰) is consistent with a magmatic origin but with a variable hydrothermal-meteoric component for the fluids, except for muscovite ($\delta^{18}O_{H,O} = -6.4\%$) and late quartz ($\delta^{18}O_{H,O} = -3.8\%$) veins, which show a dominant meteoric water component. A magmatic fluid, partly mixed with meteoric fluids ($\delta^{18}O_{qtz}$ =9.9– 10.9%; $\delta^{18}O_{H_2O}=4.13-6.95$ %; $\delta^{18}O_{mica}=4.7-5.2$ %) was involved in the genesis of the Correas deposit. The small range of variation in the $\delta^{18}O_{H_{2}O}$ values indicates re-equilibration of the fluid phase with granite at subsolidus temperatures, and CO₂-H₂O fractionation, mostly during the vein formation, in the same manner as proposed by Higgins (1985b). The isotopic temperatures calculated for the mineral pairs were in the range of 441–459 °C (quartz–cassiterite)

and 336-390 °C (quartz-wolframite), in agreement with temperatures of 300-440 °C, at fluid pressures of 1.3-2.6 kbar, respectively, obtained via fluid-inclusion microthermometry (Table 2 and Fig. 3A-C). A linear trend in δD values extending to lighter values for the same homogeneous range of δ^{18} O values is observed in the Oriente Novo and Correas deposit. Similar $\delta^{18}O/\delta D$ trends were interpreted as a result of CO₂-H₂O and CH₄-H₂O fractionation (Bottinga, 1969; Higgins, 1985b), outgassing of earlier fluids (Taylor, 1986), changing salinity in the magmatic fluids (Carten et al., 1988), minor admixture of meteoric water (Heinrich, 1990), and fluid-magma isotope effects (Rye et al., 1990), among other explanations. A contrasting $\delta^{18}O/\delta D$ behavior is observed in the Santa Bárbara deposit: the δD values for micas from greisens indicate a narrow range of variation for a wide range of δ^{18} O values, as well as deuterium enrichment in the fluids. This may reflect re-equilibration of aqueous fluid with granite at low waterrock ratios and progressively lower temperatures, as proposed by Smith et al. (1996) for similar vein fluids from the Cligga Head Sn-W deposit (southwestern England). Other explanations for similar $\delta^{18}O/\delta D$ trends at the Zaaiplaats Tin Mine (South Africa) and at the Hemerdon Ball Sn-W deposit (SW England) are provided by Pollard et al. (1991) and Shepherd et al. (1985), respectively.

8. Conclusions

The contrasting mineralization styles and fluid characteristics of the Santa Bárbara deposit in relation to the Correas and Oriente Novo deposits reflect different depths of formation, spatial relationships to tin granites and different wall rock/fluid proportions.

The fluid inclusion studies favor late-magmatic to early post-magmatic models of mineralization. The main processes involved in Sn–W mineralization are fluid-melt immiscibility, immiscibility of an original orthomagmatic CO_2 –H₂O fluid, mixture, dilution, CO_2 degassing, accompanied by hydro-fracturing, and different styles of hydrothermal alteration, mainly feldspathization, greisenization, silicification, and argilization.

The fluids associated with the mineralization are aqueous with variable concentrations of CO_2 as the

dominant volatile component. The P-T trapping conditions allow to consider two different mineralization emplacement levels: transitional from hypabyssal to plutonic, corresponding to a maximum depth of 9.8 km (Correas and Oriente Novo deposits) and at more shallow subvolcanic level, i.e., at a depth of 1.8 km (Santa Bárbara deposit).

Stable isotope and fluid inclusion data reveal three fluid types: (1) an orthomagmatic fluid, which has equilibrated with granite; (2) an orthomagmatic derived fluid mixed with hydrothermal meteoric water; and (3) a dominant late hydrothermal meteoric fluid. The first two types are responsible for cassiterite, wolframite, and columbite–tantalite precipitation. Changes in the redox conditions related to mixing of magmatic and meteoric fluids favored sulfide mineralization in Correas deposit at the post-magmatic stage.

Acknowledgements

This research was funded by FAPESP-Fundação de Amparo à Pesquisa do Estado de São Paulo (grant awarded to J.S. Bettencourt, Proc. no. 2000/08033-5, and scholarship to I. Sparrenberger, Proc. no. 1998/ 04469-1), PADCT-FINEP (research grant to J.S. Bettencourt, convênio PADCT/FINEP no. 64.99. 0276.00), and CNPq (research grant to R.M.S. Bello, Proc. no. 303872/1985-3).

We would like to express our appreciation to M. Poutiainen (Helsinki, Finland) and V.T. McLemore (Socorro, USA) for constructive and thorough reviews that improved the manuscript and R.L. Linnen (Waterloo, Canada) for his comments on the paper. We particularly thank Tapani Rämö for his fruitful suggestions, support, and invitation to contribute to this volume. The authors also thank L.V.S. Monteiro and T. Benevides for the drafts. The paper forms parts of Ph.D. studies carried out by W.B. Leite Jr., C.L. Goraieb, and I. Sparrenberger under the supervision of J.S. Bettencourt.

References

Almeida, F.F.M., Hasui, Y., Brito Neves, B.B., Fuck, R.A., 1981. Brazilian structural provinces: an introduction. Earth-Science Reviews 17, 1–29.

- Bettencourt, J.S., Leite Jr., W.B., Payolla, B.L., Scandolara, J.E., Muzzolon, R., Vian, J.A.J., 1995. The rapakivi granites of the Rondônia tin province and associated mineralization. In: Bettencourt, J.S., Dall'Agnol, R. (Eds.), Excursion Guide: The Rapakivi Granites of Rondônia Tin Province and Associated Mineralization. Symposium Rapakivi Granites and Related Rocks, Belém, Brazil. Federal University of Pará, Center for Geosciences, pp. 5–16.
- Bettencourt, J.S., Tosdal, R.M., Leite Jr., W.B., Payolla, B.L., 1999. Mesoproterozoic rapakivi granites of Rondônia tin province, southwestern border of the Amazonian craton, Brazil: I. Reconnaissance U–Pb geochronology and regional implications. Precambrian Research 95, 41–67.
- Bodnar, R.J., 1993. Revised equation and table for determining the freezing point depression of H₂O–NaCl solutions. Geochimica et Cosmochimica Acta 57, 683–684.
- Bodnar, R.J., Burnham, C.W., Sterner, S.M., 1985. Synthetic fluid inclusions in natural quartz: III. Determinations of phase equilibrium properties in the system H₂O+NaCl to 1000 °C and 1500 bars. Geochimica et Cosmochimica Acta 49, 1861–1873.
- Bottinga, Y., 1969. Calculated of fractionation factors for carbon and oxygen isotope exchange in the system calcite–CO₂–C–CH₄–H– H₂O vapor. Geochimica et Cosmochimica Acta 33, 49–65.
- Bottinga, Y., Javoy, M., 1973. Comments on oxygen isotope geothermometry. Earth and Planetary Science Letters 20, 250–265.
- Bowers, T.S., Helgeson, H.C., 1983. Calculations of the thermodynamic and geochemical consequences of nonideal mixing in the system H₂O–CO₂–NaCl on phase relations in geologic systems: metamorphic equilibria at high pressures and temperatures. American Mineralogist 68, 1059–1075.
- Brown, P.E., 1989. FLINCOR: a microcomputer program for the reduction and investigation of fluid inclusion data. American Mineralogist 74, 1309–1393.
- Brown, P.E., Lamb, W.M., 1989. P–V–T properties of fluid in the system H₂O±CO₂±NaCl: new graphical presentation and implications for fluid inclusion studies. Geochimica et Cosmochimica Acta 53, 1209–1221.
- da Campanha, G.A.C., Sadowski, G.R., 1999. Tectonics of the southern portion of the ribeira belt (apiaí domain). Precambrian Research 98, 31–51.
- Campos Neto, M.C., 2000. Orogenic systems from southwestern Gondwana: an approach to Brasiliano-Pan African cycle and orogenic collage in southearstern Brazil. In: Cordani, U.G., Milani, E.J., Thomaz Filho, A., Campos, D.A. (Eds.), Tectonic Evolution of South America 31st International Geological Congress, 2000, Rio de Janeiro, Brazil, pp. 335–365.
- Carten, R.B., Rye, R.O., Landis, G.P., 1988. Effects of igneous and hydrothermal processes on the composition of ore-forming fluids; stable isotope and fluid inclusion evidence, Henderson molibdenum deposit, Colorado. Abstracts with Programs-Geological Society of America 19, A94.
- Clayton, R.N., Mayeda, T.K., 1963. The use of bromine pentafluoride in the extraction of oxygen from silicates for isotopic analysis. Geochimica et Cosmochimica Acta 27, 43-52.

- Collins, P.C., 1979. Gas hydrates in CO₂-bearing fluid inclusions and the use of freezing data for estimations of salinity. Economic Geology 74, 1435–1444.
- Dall'Agnol, R., Costi, H.T., Leite, A.A.S., Magalhães, M.S., Teixeira, N.P., 1999. Rapakivi granites from Brazil and adjacent areas. Precambrian Research 95, 9–39.
- Davis, D.W., Lowenstein, T.K., Spencer, R.J., 1990. Melting behavior of fluid inclusions in laboratory-grown halite crystals in the systems NaCl–H₂O, NaCl–KCl–H₂O, NaCl–MgCl₂–H₂O and NaCl, CaCl₂–H₂O. Geochimica et Cosmochimica Acta 54, 591–601.
- Diamond, L.W., 1994. Introduction to phase relations of CO₂–H₂O fluid inclusions. In: De Vivo, B., Frezzotti, M.L. (Eds.), Fluid Inclusions in Minerals: Methods and Apliccations. Short Course of the Working Group (IMA) 'Inclusions in minerals'. Virginia Polytechnic Institute, pp. 131–158.
- Diamond, L.W., 2001. Review of the systematics of CO₂–H₂O fluid inclusions. Lithos 55, 69–99.
- Donnelly, T., Waldron, S., Tait, A., Dougans, J., Bearhop, S., 2001. Hydrogen isotope analysis of natural abundance and deuteriumenriched waters by reduction over chromium on-line to a dynamic dual inlet isotope-ratio mass spectrometer. Rapid Communications in Mass Spectrometry 15, 1297–1303.
- Fallick, A.E., Macaulay, C.L., Haszeldine, R.S., 1993. Implications of linearly correlated oxygen and hydrogen isotopic compositions for kaolinite and illite in the Magnus sandstone, North Sea. Clays and Clay Minerals 41, 184–190.
- Fifarek, R.H., 1985. Alteration geochemistry, fluid inclusion, and stable isotope study of the Red Ledge volcanogenic massif sulfide deposits, Idaho. Ph.D. thesis, Oregon State University, U.S.A.
- Frank, R.E., 1990. Geologia, petrologia e mineralizações estaníferas do Complexo Granítico de Santa Bárbara, Rondônia, Brasil. M.Sc. thesis, Instituto de Geociências, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil (in Portuguese).
- Gilg, H.A., Sheppard, S.M.F., 1996. Hydrogen isotope fractionation between kaolinite and water revisited. Geochimica et Cosmochimica Acta 60, 529–533.
- Gimenez Filho, A., de Janasi, V.A., da Campanha, G.A.C., Teixeira, W., Trevizoli Jr., L.M., 2000. U–Pb dating and Rb–Sr isotope geochemistry of the eastern portion of the Três Côrregos batholith, Ribeira fold belt, São Paulo. Brazilian Contributions to 31st International Geological Congress, Rio de Janeiro, Brazil, Revista Brasileira de Geociências 30, pp. 45–50.
- Goraieb, C.L., 2001. Contribuição à gênese do depósito primário polimetálico (Sn, W, Zn, Cu, Pb) Correas, Ribeirão Branco (SP). Ph.D. thesis, Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil (in Portuguese).
- Haapala, I., 1997. Magmatic and postmagmatic processes in tinmineralized granites: topaz-bearing leucogranite in the eurajoki rapakivi granite stock, Finland. Journal of Petrology 38 (12), 1645–1659.
- Hedenquist, J.W., Henley, R.W., 1985. The importance of CO₂ on freezing point measurements of fluid inclusions: evidence from active geothermal systems and implications for epithermal ore deposition. Economic Geology 80, 1379–1406.
- Heinrich, C.H., 1990. The chemistry of hydrothermal tin (-tungsten) ore deposition. Economic Geology 85, 457–481.

- Heyen, N.C., Ramboz, C., Dubessy, J., 1982. Simulations des équilibres de phases dans le système CO₂–CH₄ en dessous de 50 °C et de 100 bar: application aux inclusions fluids. Comptes Rendus de la Académie des Sciences, Paris 294, 203–206.
- Higgins, N.C., 1985a. Wolframite deposition in a hydrothermal vein system: the grey river tungsten prospect, Newfoundland, Canada. Economic Geology 80, 1297–1327.
- Higgins, N.C., 1985b. Moderately depleted oxygen isotope composition of waters associated with tin-and tungsten-bearing quartz veins: an evaluation of isotopic models. In: Herbert, H.K., Ho, S.E. (Eds.), Conference on Stable Isotopes and Fluid Processes in Mineralization, Queensland, 1985. Geology Department and University Extension of the University of Western Australia Publication, vol. 23, pp. 204–214.
- de Janasi, V.A., Ulbrich, H.H.G.J., 1991. Late proterozoic granitoid magmatism in the state of São Paulo, Southeastern Brazil. Precambrian Research 51, 351–374.
- Jenkin, G.R.T., 1998. Stable isotope studies in the Caledonides of S.W. Connemara, Ireland. Glasgow, Ph.D. thesis, University of Glasgow, United Kingdom.
- Kloosterman, J.B., 1970. A two fold analogy between the Nigerian and Amazonian tin provinces. Technical Conference on Tin 2, Bangkok, vol. 1, pp. 193–221.
- Leite, W.B. Jr., 2002. A Suíte Intrusiva Santa Clara (RO) e a mineralização primária polimetálica (Sn, W, Nb, Ta, Zn, Cu e Pb) associada. Ph.D. Thesis, Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil (in Portuguese).
- Leite Jr., W.B., Payolla, B.L., Bettencourt, J.S., 2000. Petrogenese of two Grenvillian tin-bearing rapakivi suites in the Rondônia tin province, SW Amazonian craton, Brazil. The 31st International Geological Congress, Rio de Janeiro, Brazil, Abstracts volume, Rio de Janeiro. Geological Survey, Brazil. [CD-ROM].
- Leite Jr., W.B., Bettencourt, J.S., Payolla, B.L., 2001. 1.08–1.07 Ga A-type granite magmatism in the Rondônia tin province, SW Amazonian craton, Brazil: petrologic and geochemical constraints. Abstracts, vol. 26. Geological Association of Canadá/ Mineralogical Association of Canadá Joint Annual Meeting, St John's, Newfoundland, Canadá, p. 85.
- Linnen, R.L., 1998. Depth of emplacement, fluid provenance and metallogeny in granitic terranes: a comparison of western Thailand with other tin belts. Mineralium Deposita 33, 461–476.
- Manning, D.A.C., 1982. An experimental study of the effects of fluorite on the crystallization of granitic melts. In: Evans, A.M. (Ed.), Metallization Associated with Acid Magmatism. John Wiley, Chichester, pp. 191–203.
- Matsuhisa, Y., Goldsmith, J.R., Clayton, R.N., 1979. Oxygen isotopic fractionation in the system quartz-albite-anorthitewater. Geochimica et Cosmochimica Acta 43, 1131–1140.
- Mcaulay, C.L., Fallick, A.E., Haszeldine, R.S., Graham, C.M., 2000. Methods of laser-based stable isotope measurement applied do diagenetic cements and hydrocarbon reservoir quality. Clay Minerals 35, 313–322.
- O'Neil, J.R., Taylor, H.P., 1967. The oxygen isotope and cation exchange chemistry of feldspars. American Mineralogist 52, 1414–1437.

384

- Payolla, B.L., Bettencourt, J.S., Kozuch, M., Leite Jr., W.B., Fetter, A.H., Van Schmus, W.R., 2002. Geological evolution of the basemente rocks in the east-central part of the Rondônia tin province, SW Amazonian craton, Brazil: U–Pb and Sm–Nd isotopic constraints. Precambrian Research 119, 141–169.
- Pimentel, M.M., Heaman, L., Fuck, R.A., Marini, O.J., 1991. U–Pb zircon geochronology of precambrian tin-bearing continental type acid magmatism in central Brazil. Precambrian Research 52, 321–335.
- Pollard, P.J., 1989a. Geochemistry of granites associated with tantalum and niobium mineralization. In: Möller, P., Černý, P., Saupé, F. (Eds.), Lanthanides, Tantalum and Niobium. Springer-Verlag, Berlin, pp. 145–158.
- Pollard, P., 1989b. Geologic characteristics and genetic problems associated with the development of granite-hosted deposits of tantalum and niobium. In: Möller, P., Černý, P., Saupé, F. (Eds.), Lanthanides, Tantalum and Niobium. Springer-Verlag, Berlin, pp. 240–256.
- Pollard, P.J., Andrew, A.S., Taylor, R.G., 1991. Fluid inclusion and stable isotope evidence for interaction between granites and magmatic hydrothermal fluids during formation of disseminated and pipe-style mineralization at the zaaiplaats tin mine. Economic Geology 86, 121–141.
- Potter III, R.W., Clyne, M.A., Brown, D.L., 1978. Freezing point depression of aqueous sodium chloride solutions. Economic Geology 73, 284–285.
- dos Prazeres Filho, H.J., 2000. Litogeoquímica, Geocronologia (U– Pb) e Geologia Isotópica dos Complexos Graníticos Cunhaporanga e Três Córregos, Estado do Paraná. M.Sc. thesis, Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil (in Portuguese).
- Priem, H.N.A., Bon, E.H., Verdurmen, E.A.T., Bettencourt, J.S., 1989. Rb–Sr chronology of precambrian crustal evolution in Rondônia (western margin Brasilian craton). Journal of South American Earth Sciences 2, 163–170.
- Ramboz, C., Pichavant, M., Weisbrod, A., 1982. Fluid immiscibility in natural processes: use and misuse of fluid inclusion data; II: interpretation of fluid inclusion data in terms of immiscibility. Chemical Geology 37, 29–48.
- Rieder, M., Cavazzini, G., D'Yakonov, Y., Frank-Kamenetskii, V.A., Gottardi, G., Guggenheim, S., Koval, P.V., Müller, G., Neiva, A.M.R., Radoslovich, E.W., Robert, J.-L., Sassi, F.P., Takeda, H., Weiss, Z., Wones, D.R., 1998. Nomenclature of the micas. The Canadian Mineralogist 36, 905–912.
- Roedder, E., 1984. Fluid Inclusions. Reviews in Mineralogy vol. 12. Mineralogical Society of America.
- Rye, R.O., Lufkin, J.L., Wasserman, M.D., 1990. Genesis of the rhyolite-hosted tin ocurrences in the black range, New Mexico, as indicated by stable isotope studies. Geological Society of America Special Paper 246, 233–250.
- Scandolara, J.E., Rizzotto, G.J., Bahia, R.B.C., Quadros, M.L.E.S, Amorim, J.L., Dall'Igna, L.G., 1999. Geologia e Recursos Minerais do Estado de Rondônia: texto explicativo e mapa geológico na escala 1:1,000,000. Programa Levantamentos Geológicos do Brasil. CPRM-Serviço Geológico do Brasil, Brasília, Brazil. In Portuguese.

- Shepherd, T.J., Miller, M.F., Scrivener, R.C., Darbyshire, D.F.P., 1985. Hydrothermal fluid evolution in relation to mineralization in southwest England with special reference to the dartmoorbodmin area. High heat production (HHP) granites, hydrothermal circulation and ore genesis. The Institution of Mining and Metallurgy, London, pp. 345–364.
- Sheppard, S.M.F., 1986. Characterization and isotopic variations in natural waters. In: Valley, J.W., Taylor, H.P., O'Neil, J.R. (Eds.), Stable Isotopes in High Temperature Geological Processes, Reviews in Mineralogy, vol. 16. Mineralogical Society of America, pp. 165–183.
- Sheppard, S.M.F., Gilg, H.A., 1996. Stable isotope geochemistry of clay minerals. Clay Minerals 31, 1–24.
- Smith, M., Banks, D.A., Yardley, B.W.D., Boyce, A., 1996. Fluid inclusion and stable isotope constraints on the genesis of the cligga head Sn–W deposit, S.W. England. European Journal of Mineralogy 8, 961–974.
- Sparrenberger, I., 2003. Evolução da mineralização primária estanífera associada ao maciço granítico Santa Bárbara, Rondônia. Ph.D. thesis, Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil (in Portuguese).
- Sun, S., Yu, J., 1992. Euhedral crystals of quartz in Ta-granite: eocrystal, not porphyroblastic. 29th International Geological Congress, Kyoto, Japan, 1992. Abstracts, vol. 2. IUGS, Kyoto, p. 539.
- Suzuoki, T., Epstein, S., 1976. Hydrogen isotope fractionation between OH-bearing minerals and water. Geochimica et Cosmochimica Acta 40, 1229–1240.
- Taylor Jr., H.P., 1979. Oxygen and hydrogen isotope relationships in hydrothermal mineral deposits. In: Barnes, H.L. (Ed.), Geochemistry of Hydrothermal Ore Deposits, 2nd ed. John Wiley and Sons, New York, pp. 236–277.
- Taylor, B.E., 1986. Magmatic volatiles; isotopic variation of C, H, and S. In: Valley, J.W., Taylor Jr., H.P., O'Neil, J.R. (Eds.), Stable Isotopes in High Temperature Geological Processes, Reviews in Mineralogy, vol. 16. Mineralogical Society of America, pp. 185–220.
- Taylor, R.P., 1992. Petrological and geochemical characteristics of the pleasant ridge zinnwaldite-topaz granite, southern New Brunswick, and comparisons with other topaz-bearing felsic rocks. Canadian Mineralogist 30, 895–921.
- Taylor, R.P., Fallick, A.E., 1997. The evolution of fluorine-rich felsic magmas: source dichotomy, magmatic convergence and the origins of topaz granite. Terra Nova 9 (3), 105–108.
- Ulbrich, H.H.G.J., Janasi, V., Vlach, S.R.F., 1991. Contrasted granitoid occurrences with rapakivi affinities in basement areas of the states of São Paulo and Minas Gerais, southeastern Brazil. In: Haapala, I., Rämö, O.T. (Eds.), Abstract Volume, Symposium on Rapakivi Granites and Related Rocks, IGCP Project 315, Guide-Geological Survey of Finland vol. 34, p. 54.
- Vlach, S.R.F., de Janasi, V.A., Vasconcellos, A.C.B.C., 1990. The Itu belt: associated calc-alkaline and aluminous A - type late Brasiliano granitoids in the states of São Paulo and Paraná, southern Brazil. Congresso Brasileiro de Geologia 36,1990, Natal, Anais Natal SBG, vol. 4, pp. 1700–1711.
- Wernick, E., 1992. Rapakivi granites related to post-collisional relaxing stage: the Itu province (late precambrian) of SE Brazil.

29th International Geological Congress, Kyoto, Japan, 1992. Abstracts, vol. 2. IUGS, Kyoto, p. 563.

- Wernick, E., Godoy, A.M., Galembeck, T.M.B., 1991. The São Francisco, Sorocaba and Itu rapakivi complexes (late precambrian, state of São Paulo, Brazil): geological, petrographic and chemical aspects. In: Haapala, I., Rämö, O.T. (Eds.), Abstract Volume, Symposium on Rapakivi Granites and Related Rocks, IGCP Project 315, Guide-Geological Survey of Finland, vol. 34, pp. 61–62.
- Wernick, E., Galembeck, T.M.B., Godoy, A.M., Hörmann, P.K., 1997. Geochemical variability of the rapakivi Itu rovince, state of São Paulo, SE Brazil. Anais da Academia Brasileira de Ciências 69, 395–413.
- Wilkinson, J.J., 2001. Fluid inclusions in hydrothermal ore deposits. Lithos 55, 229–272.

- Zhang, L.G., Zhuang, L., Quian, Y., Guo., Y., Qu, P., 1982. Stable isotope geochemistry of granites and tungsten-tin deposits in Xihuashan - Piaotang area, Jiangxi Province. Tungsten Geol. Symposium, Jiangxi, China. ESCAP RMRDC, Bandung, Indonesia. Geological Publishing House, Beijing, China, pp. 553–566.
- Zhang, L.G., Liu, J.X., Chen, Z.S., Zhou, H.B., 1994. Experimental investigations of oxygen isotope fractionation in cassiterite and wolframite. Economic Geology 89, 150–157.
- Zheng, Y.F., 1993a. Calculation of oxygen isotope fractionation in anhydrous silicate minerals. Geochimica et Cosmochimica Acta 57, 1079–1091.
- Zheng, Y.F., 1993b. Calculation of oxygen isotope fractionation in hydroxyl-bearing silicates. Earth and Planetary Science Letters 120, 247–263.

386