The Santa Rita gold deposit in the Proterozoic Paranoá Group, Goiás, Brazil: An example of fluid mixing during ore deposition

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ABSTRACT

The Santa Rita gold deposit (Central Goiás, Brazil) is hosted by Middle to Upper Proterozoic carbonate-pelite sequences of the Paranoá Group that have been metamorphosed in the greenschist facies. The ore is contained in pyritebearing quartz-carbonate veins. The mineralization is structurally controlled by WNW-ESE high-angle faults and fractures resulting from the reactivation of older NE-SW lineaments. Pyrite is the sole sulphide and it shows growth zones enriched in Co, Ni and As (up to 4 wt%). Hydrothermal alteration zones are enriched in Co, Ni and As and are characterized by diffuse albitization, carbonatization, silicification and pyritization.

A fluid inclusion study on quartz from pyrite-bearing quartz-carbonate veins led to the identification of two fluids: (1) a highly saline CO_2-N_2 -rich aqueous fluid with halite and \pm sylvite daughter minerals, and (2) a CO_2-N_2 rich aqueous fluid with moderate salinity. The two fluid types occur in the same quartz domain and display great variation in the degree of filling and notable dispersion of the microthermometric data. On heating, all the inclusions decrepitate between 200° and 300°C. Raman spectrometry detected high concentrations of N₂ in the gas phase, with a CO_2/N_2 molar ratio between 1 and 19 and a small proportion of CH₄ (up to 2 mole %).

The simultaneous entrapment of compositionally variable fluids in the system $H_2O-CO_2-N_2-NaCl-KCl$ allow us to propose a mechanism of heterogeneous trapping. The entrapment may result from the mixing of a high-salinity fluid ($H_2O-NaCl-KCl$ system) with a carbonic fluid ($H_2O-CO_2-N_2$ system) produced by the devolatilization process of carbonate and phyllitic host rocks. Considering the absence of spatially and temporally related igneous activity and the low P-T regional metamorphism in the Paranoá Group, the brines are inferred to result from leaching of evaporites occurring in the lower part of the Paranoá lithostratigraphic column.

Gold was probably initially transported as an AuCl₂-complex $(T > 300^{\circ}C)$, low pH, moderate f_{O_2} -pyrite field stability). As temperature decreased below 290°C, the "switch-over" process** would lead to the predominance of Au(HS)₂⁻ in the fluid. Pyrite precipitated in this temperature interval. The oscillatory zoning of the As-Co-Ni-bearing pyrites indicates episodic fluctuation of the fluid composition. Such changes in fluid composition are favoured by a mechanism of fluid mixing by intermittent supplies in the hydrothermal system. The proposed mechanism of heterogeneous trapping of two separate fluids in the system H₂O-CO₂-N₂-NaCl-KCl and the resulting changes in the physicochemical conditions caused by the fluid mixing appears as a conspicuous process for the Santa Rita hydrothermal fluid evolution.

A model based on the existence of a Proterozoic geothermal system involving the regional thermal gradient is proposed.

Introduction

The State of Goiás in Central Brazil hosts several gold mining districts which are locate-

din different geological and structural environments. Important and well-known Goiás gold deposits belong to the Crixás mineral province (Kishida et al., 1990). These deposits are hosted within Archaean greenstone belts and are spatially associated with major shear zones (Leonardos et al., 1988). Generally, the

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Fig. 1. For caption see p. 505.

mineralized structures are characterized by multi-stage ore deposition in sulphide-quartz veins and/or sulphide disseminations in mylonitic and ultramylonitic rocks related to shear zones (Pulz et al., 1991a).

In addition to these Archaean-hosted gold concentrations, Goiás contains metasedimentary Proterozoic gold deposits that occur in regional overthrust belt structures (Haggemann et al., 1988, 1992; Olivo, 1989). In this case, the low-grade ore (Lacerda, 1991) is contained in sulphide-bearing quartz veins and gold is mainly associated with pyrite.

Our understanding of greenstone gold deposits and hydrothermal gold mineralization related to Precambrian terranes has increased considerably throughout the world during the last decade (Keays and Skinner, 1989; Ho et al., 1990; Robert et al., 1990). These deposits occur over a wide range of metamorphic grades and crustal levels, and are spatially associated with major crustal fault zones that acted as fluid channelways. Many factors control ore deposition in these major tectonic structures, such as structural traps, and permeability and composition of the surrounding rocks, but fluid pressure appears to be the predominant factor (Sibson et al., 1988).

Fluids are of great importance in the genetic modelling of hydrothermal gold deposits. The chemistry of the hydrothermal solutions transporting and precipitating gold, as well as the nature of the gold complexes in these fluids are of special interest (Seward, 1973; Romberger, 1986; Shenberger and Barnes, 1989). The mechanism of gold deposition and fluid degeneration in mineralized structures are generally discussed in terms of fluid immiscibility or unmixing (Robert and Kelly, 1987; Williams-Jones and Ferreira, 1989; Guha et al., 1991), or more rarely of fluid mixing (Boiron et al., 1990). These recent studies emphazise the importance of fluid inclusion studies to gain knowledge of the nature and composition of ore fluids.

During the last ten years, new data on structural setting (Angeiras et al., 1988), *P-T* environment (Thomson and Fyfe, 1990) and control of mineralization (Kuyumjian and Dardenne, 1983; Richardson et al., 1986; Magalhães et al., 1988) have been collected on the Goiás gold deposits. But the nature and composition of gold-bearing fluids, as well as modelling on the source of the auriferous fluids have received little attention until now (Giuliani et al., 1991a,b; Fortes and Giuliani, 1992).

The purpose of this study is to characterize the chemical composition of the fluid phases associated with the Santa Rita gold deposit (Central Goiás, Fig. 1). In order to address the problem, we carried out microthermometric analyses on quartz from pyrite-bearing, quartzcarbonate veins. The knowledge of bulk composition and density of the different fluid phases allowed us to constrain the factors controlling the transport and deposition of gold during the evolution of a hydrothermal system developed in the Paranoá Proterozoic sequence.

Fig. 1. Geological sketch map of the state of Goiás showing the localization of the different greenstone belts and the main gold deposits. Greenstone belts: I=Goiás; II=Crixás; III=Pilar de Goiás/Hidrolina, IV=Mara Rosa. Gold deposits related to shear zones affecting the Archaean granite-gneissic basement (2=Auromina; I6=Aurilândia), greenstone belts (8=Mara Rosa; I0=Campinorte; II=Pilar de Goiás; I2=Guarinos; I3=Crixás with the mines of Meia Pataca, Mina III, Chapeu do Sol; I4=Goiás), and Middle to Upper Proterozoic formations (I=São Domingos; 3=Cavalcante; I7=Jaraguá-Pirenópolis). Gold deposits related to regional overthrust belt structures within the Middle to Upper Proterozoic (4=Rio do Carmo district; 5=Santa Rita gold deposit 6=Niquelândia district; 7=Uruaçu, I8=Luziânia). Other types of gold deposits: Porphyry Cu-Au type (9=Chapada) and Witwatersrand gold type (I5=Morro da Lavra). 19 corresponds to the Morro do Ouro gold deposit (Minas Gerais State) with indicated reserves of 50×10^6 tons of ore at 0.6 g/t (Zini et al., 1988).

Precambrian gold deposits of Goiás***

The Precambrian of Goiás

The gold deposits are hosted by Archaean and Proterozoic rocks (Fig. 1) that belong to the Tocantins Province (Almeida et al., 1977).

The Precambrian of Goiás is composed of: (1) an Archaean basement with remnants of Lower Proterozoic metasedimentary sequences, (2) Lower Proterozoic gabbro-anorthositic complexes and volcanosedimentary sequences, and (3) Middle to Upper Proterozoic Fold Belts (Marini et al., 1984).

(1) the Archaean comprises a granite-gneiss complex and several greenstone belts. The main greenstone belts are, from south to north (Fig. 1), the Goiás, Crixás, Pilar de Goiás/ Hidrolina and Mara Rosa belts (Danni, 1988), respectively. Generally, they are composed of basal ultramafic metavolcanics, an intermediate to mafic (with minor felsics) metavolcanic formation and, on top, detrital and chemical metasediments. However, the assigned Archaean age of the Mara Rosa volcanosedimentary sequences is always in debate, and Richardson et al. (1986) proposed a Proterozoic age for the Mara Rosa metavolcanics, based on Rb/Sr whole rock isochron.

(2) The Lower Proterozoic is composed of gabbro-anorthositic complexes and a metavolcanosedimentary series (amphibolite facies) which contain mafic metavolcanics and pelitic metasedimentary formations.

(3) the Middle to Upper Proterozoic fold belts are represented by the Uruaçu (1300– 1000 Ma) and Brasília fold belts (900–500 Ma), respectively. The first belt (Fig. 1) is composed of metasediments, metamorphosed to amphibolite-greenschist facies, that define the Araxá, Araí and Serra da Mesa groups (Marini et al., 1984). The Brasília fold belt contains low-grade metamorphosed metasediments with a predominance of quartzite and limestone. These rocks correspond to the Paranoá and Bambuí groups, and the Canastra and Vazante formations (Fig. 1).

A series of tin-bearing granitoidic complexes intrude both Archaean and Middle Proterozoic metasediments (Marini and Botelho, 1986).

The Precambrian gold deposits of Goiás

A large number of Goiás gold deposits are directly associated with shear zones (Lacerda, 1991; Leonardos et al., 1991; Marini and Queiroz, 1991) that affect (1) Archaean granite-gneissic basement, and/or (2) greenstone belts, and (3) Proterozoic formations.

(1) In the Archaean granite-gneissic basement, gold is found mainly as native gold in sulphide-bearing quartz veins and veinlets in mylonites and ultramylonites. The quartz veins range from centimetres to metres in thickness, are tens to hundreds of metres long and are about 100 m deep. Concentrations of this type (Fig. 1) are found in Auromina (Au, Pb, Zn association) which contains proven reserves of 86.000 t ore at an average grade of 5.8 g/t, and in the Aurilândia deposits (reserves of 500.000 t at 5.4 g/t);

(2) The greenstone belts belong to the typical greenstone-type gold deposit described by Robert et al. (1990). These deposits are associated with intense hydrothermal alteration of metabasic volcanics (propilitization, albitization, carbonatization, sericitization and tourmalinization; Pulz et al., 1991b) and developed along compressive or dilatency locations of shear zones. Orebodies occur either as disseminated sulphides in mylonitic zones, controlled by stretching lineation (Magalhães et al., 1988), or as high-grade native gold-bearing quartz veins (Fortes and Nilson, 1990). These deposits are exploited either by mining companies as in Crixás (Mina III deposit, reserves of 5.300,000 t at 12.72 g/t; Meia Pataca, re-

^{***}A gold deposit is defined as a gold concentration explored by mining company, prospectors or the XVIII century Bandeirantes workers.

serves of 22.400 t at 2.98 g/t), Mara Rosa (182.000 t at 2.08 g/t; Angeiras et al., 1988), or by prospectors called "garimpeiros" as in the Guarinos (Pulz et al., 1991a), Crixás (Chapeu do Sol, Au-Pb-Zn association), and the Goiás and Pilar de Goiás deposits.

(3) The Proterozoic is composed of a series of gold deposits, hosted in the Middle to Upper Proterozoic Uruaçu fold belt, located in detrital metasediments (Jaraguá-Pirenopólis, Cavalcante and São Domingos; Fig. 1).

In addition to gold deposits related to shear zones, a second type of gold concentration occurs within the Brasília fold-thrust belt at the western border of the São Francisco craton (Fig. 1). Gold is found in phyllite, carbonate or quartzite, either as native metal, or associated with sulphides in boudinaged quartz veinlets. This type of gold concentration is mined by prospectors in the districts of Rio do Carmo, Niquelandia (Lacerda and Pereira, 1988; Olivo and Marini, 1988); reserves are unknown. However, these deposits are low grade with erratic enrichments up to 60 g/t (Lacerda, 1991).

Two other types of deposits are known in Goiás: (1) the Chapada Cu-Au deposit (Fig. 1), located within the Mara Rosa greenstone belt with an extensive $(134 \times 10^{6} t)$, low grade (0.44% Cu; 0.35 g/t Au) concentration of metal (Richardson et al., 1986). It is considered by the authors to be a metamorphosed porphyry copper deposit, hosting mineralization in both wall-rocks and intrusive diorites. It represents the only Precambrian porphyry Cu-Au deposit known in Central Brazil. (2) The Morro da Lavra deposit overlies the Goiás greenstone belt. It corresponds to a Witwatersrand type of gold deposit located in metaconglomerates (greenschist facies) of the lower part of an early Proterozoic metasedimentary sequence (Serra da Santa Rita Formation). This deposit was explored during the XVIII century by the Bandeirantes.

The Middle to Upper Proterozoic Paranoá Group

Geology

The Middle to Upper Proterozoic Paranoá group (Fig. 2) occurs within the Brasília Belt in the Tocantins Province (Marini et al., 1984). It consists of ten mappable units grouped in two sequences (Olivo and Marini, 1988): (1) a psammitic-pelitic sequence (units A, B, C, D, E; Fig. 3) and (2) a carbonatepsammitic-pelitic sequence (units F,G,H,I,J).

In the western part of the region, the Paranoá group is limited by a regional thrust verging east and is characterized by thrusting of



Fig. 2. Distribution of the psammitic-pelitic and carbonate-psammitic-pelitic sequences of the Paranoá Group in Central Goiás, with the localization of the Rio do Carmo and Niquelândia gold mining districts with the Santa Rita gold deposit.



Fig. 3. Lithostratigraphic column of the Paranoá Group showing the stratigraphic position of the different gold deposits of the Rio do Carmo and Niquelândia mining districts. I=lateritic gold deposits (supergene enrichment); 2=primary gold deposits.

Archaean and Lower to Middle Proterozoic sequences over the Paranoá group. To the east, in the region of Alto Paraiso and São João da Aliança (Fig. 2), the thrust structure results in the overlying of the Paranoá group on the Upper Proterozoic Bambuí formations. In the region of the Rio Paranã, the basal Paranoá sequence lies uncomformably over the Middle Proterozoic Araí group.

Well-defined sedimentary, tectonic and metamorphic polarities show a cratonic area in the eastern part of the region. The metamorphic polarity is clear: the metamorphic grade decreases from the west (greenschist facies) to the east (anchimetamorphic zone). Primary sedimentary structures (as evaporites levels; see Fig. 3) within the phyllites of the sequence (1) are well preserved (Dardenne and Faria, 1985).

Paranoá gold deposits

The Paranoá gold deposits are distributed within sequence (2) and in unit E of sequence (1), where the sediments of the Paranoá group were metamorphosed under greenschist facies conditions (up to the biotite zone; see Fig. 2). Gold mineralization is structurally controlled by faults and fractures which are reactivated older NE-SW lineaments, such as the Niquelandia-Campos Belos and Minaçu-Cana Brava structures (Fig. 2). These structures crosscut the Lower Proterozoic Niquelandia and Cana Brava basic and ultrabasic massifs (Olivo and Marini, 1988).

The gold deposits form two auriferous districts, i.e., Rio do Carmo and Niquelandia (Fig. 2). These districts are mined by prospectors, reserves are unknown. Primary gold concentrations are contained in sulphide-bearing quartz veins in phyllites and quartzites, or in sulphide-bearing quartz-carbonate veins in metamorphosed limestones and dolomites. The gold-bearing quartz veins range in thickness from centimetres to metres and are tens of metres along strike. The main sulphides are pyrite, pyrrhotite, arsenopyrite and chalcopyrite. Fire assays indicate gold grade up to 60 ppm (Lacerda, 1986).

The Santa Rita gold deposit

Geological setting

The Santa Rita area is situated in the upper part of unit E (rythmic sequence of carbon-rich quartzite, phyllite and muscovite phyllite) and unit F (rythmic sequence of quartzite, quartz phyllite, muscovite phyllite and levels of metadolomites and metalimestones with intercalated calciphyllites at the top). In this region, four phases of folding are recognized (Olivo, 1989): (a) the first two phases correspond to isoclinal folding with a well-developed planar axial schistosity; (b) the third phase is characterized by closed and frequently assymetric folds with north-south-trending fold axes; (c) the fourth phase corresponds to gentle open folds with axes oriented WNW-ESE. These folding events are followed by NNW- and NEtrending faulting and later WNW-ESE-trending fractures to which the mineralized structures are related.

The ore is contained in sulphide-bearing quartz-carbonate veins and veinlets enclosed in pelitic-psammitic-carbonatic rocks of unit F (Fig. 3). The mineralization is structurally controlled by WNW-ESE-trending high-angle faults and fractures, which are the result of a reactivation of older NE-SW structures related to the Niquelandia-Campos Belos lineament (Olivo, 1989).

The veins are 1 cm to 1 m thick with a lateral extension of tens of metres. They consist of quartz accompanied by Fe-dolomite, ankerite, calcite and sulphides. Pyrite is the main sulfide phase; it is occasionally accompanied by rare inclusions of chalcopyrite and pyrrhotite. Native gold is not observed and gold grades vary between 0.1 and 10 ppm, locally reaching 60 ppm.

The mineralization is related to a restricted zone of fluid circulation. Fluids percolated along the faults and fractures provoking diffuse and limited hydrothermal alterations as albitization, carbonatization, silicification, sericitization and pyritization. The hydrothermal zones are enriched in Co, Ni and As (Olivo, 1989).

Albitization and sericitization are developed within the metalimestones and metadolomites. Albite occurs as large crystals often bordered by a sericitic margin. Sericite also occurs as disseminated grains throughout the carbonate rocks.

The carbonate alteration is marked by the formation of veins and veinlets of Fe-dolomite and ankerite which are crosscut by latter calcite veins. The Fe-bearing carbonates are impregnated by carbonaceous matter; calcite also occurs as poikiloblasts within psammitic-pelitic rocks.

Silicification is represented by quartz veins with a length of a few centimeters to meters and are probably contemporaneous to albitization and sericitization processes.

Oscillatory-zoned As-Co-Ni-bearing pyrites

Pyrite from quartz-carbonate veins has been examined by scanning electron microscopy (SEM) and analyzed by quantitative electron microprobe (QEM).

QEM analyses were performed on a Cameca SX microprobe (University of Nancy) under the following analytical conditions: accelerating voltage: 30 kV, 60 nA; counting time: 30 s for Co, Ni, Ag, Au, As, Sb, and 10 s for Fe, S. The detection limit for gold is 800 ppm under these analytical conditions.

Backscattered SEM images show crystals of pyrite with oscillatory zoning (Fig. 4). This growth zoning is characterized by alternating white coloured-areas and dark-contrasted zones. QEM analyses (Table 1) of the white growth zones, show enrichment in As–Co and Ni, which correlate with a decrease in S. Asenrichment is closely related to an increase of Co. All pyrite grains have irregular and apparently corroded As-margin zones, and regular zoned crystals with zoning parallel to the crystal faces are rare. The Co and Ni contents vary

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Fig. 4. Backscattered SEM images of pyrites showing the zoning of different grains. Zoning is materialized by the alternation of white coloured zones enriched in As, Co and Ni (points 2, 3, 4, 8, see analyses of Table 1) and dark areas (points 1, 5, 6, 7, 9). (The horizontal and regular white band which crosscuts all the grains is an image defect due to SEM image equipment.)

TABLE 1

Quantitative electron microprobe analysis of a zoned pyrite grain from Santa Rita pyrite-bearing quartz-carbonate veins

Zone	1	2	3	4	5	6	7	8	9
As	0.05	1.88	2,09	1.44	0.55	0.03	0.24	1.56	0.52
Fe	45.67	44.33	44.86	44.53	45.54	45.90	46.21	45.14	45.32
S	53.52	52.43	51,90	52.19	53.21	53.48	52.97	52.36	53.46
Co	0.41	0.39	0.42	0.55	0.25	0.25	0.21	0.39	0.65
Ni	0.00	0.51	0.56	0.37	0.06	0.00	0.00	0.42	0.00
Total	99.65	99.54	99.83	99.08	99.61	99.66	99.63	99.87	99.95
As	0.03	1.02	1.13	0.78	0.29	0.02	0.13	0.84	0.28
Fe	32.82	32.14	32.57	32.41	32.78	32.78	33.28	32.65	32.57
S	66.98	66.22	65.63	66.17	66.71	66.87	66.45	65.95	66.91
Co	0.1	0.27	0.29	0.38	0.17	0.17	0.14	0.27	0.22
Ni	0.00	0.35	0.38	0.26	0.04	0.00	0.00	0.29	0.02

Each analysis (with the results in wt% and atomic concentrations) corresponds to the points indicated in Fig. 4 (points 1-9).

from 0-4.09 wt% and from 0-0.55 wt%, respectively. The zoning is more or less distinct, following the As content of the zone which varies between 0.48 and 4.18 wt%.

Gold in pyrite is under the detectable limit

of QEM. LMA-10 laser microanalyzes indicate values around 100 ppm and confirm the auriferous character of the pyrite. Gold exists probably in a combined chemical state in the As-zoning of pyrites (Marion et al., 1991). The rare inclusions of pyrrhotite and chalcopyrite in pyrite do not show any zoning; traces of Co, Ni, As, and Au are not found.

Fluid inclusions study of the Santa Rita gold deposit

Analytical methods

Fluid inclusions (FI) in ten milky quartz samples representative of the pyrite-bearing quartz-calcite veins were studied by microthermometry, SEM and Raman spectrometry.

Microthermometric studies were carried out using a Chaix-Meca heating-freezing stage (Poty et al., 1976) on 200-300 μ m thick, doubly-polished plates. The low-temperature range measurements were obtained with a precision of 0.1 °C. The high temperature measurements were performed by heating the inclusions at a rate of 1 °C per min. The accuracy was estimated at \pm 1 °C between 50° and 300°C.

The following symbols are used in the text and in the figures. DF=degree of filling of FI at room temperature; T_m =temperature of final melting of CO₂ (solid CO₂), i (ice H₂O), C (clathrate=gas hydrate); T_h =temperature of homogenization of CO₂ (l: liquid; v: vapor; c: critical); T_H =total homogenization of the inclusion (l: liquid; v: vapor; c: critical); T_D =temperature of decrepitation; T_{sNaCl} and T_{sKCl} = dissolution temperature of halite and sylvite, respectively; d_{vapor} =carbonic-phase density (g/cm³); NaCl (wt%) = salinity of the inclusion.

Qualitative analysis of the solid phases contained in the cavity of FI were performed on a Cambridge Stereoscan 250 SEM, operating at an accelerating voltage of 20 kV.

Molar fractions of the volatiles in the gas phase of individual FI were measured on a Dilor X-Y multichannel laser-excited Raman spectrometer, using the 514.5 nm radiation of an Ar ion laser. The presence of the volatile phases CO₂, CH₄, N₂ and H₂S was checked using a 1 W laser beam referring to the following lines, respectively: 1388 cm^{-1} and 1285 cm^{-1} , 2915 cm⁻¹, 2331 cm⁻¹ and 2611 cm⁻¹.

Petrography and relative chronology of the fluid inclusions

Two main types of FI are recognised in the samples, on the basis of their relative phase proportions (vapour-to-liquid and solid ratio) estimated at room temperature (Fig. 5):

Type I: Two- and three-phase, CO₂-rich inclusions (H₂O_L and CO_{2L+V}) which can be divided in two subtypes considering the volumetric proportions of the H₂O and CO₂-rich phases: Subtype IA with a degree of filling (*DF*) representing 5-40% of the total volume of FI and Subtype IB with 55 < DF < 90% (Fig. 6A).

Type II: Multiphase solid, CO_2 -rich inclusions (H_2O_L and CO_{2L+V}) with halite daughter mineral (10–15% of the total volume of FI) with sometimes sylvite. Two subtypes are also



Fig. 5. Typical distribution of fluid inclusions observed in a quartz plate (sample PSR 7-6) from the Santa Rita gold deposit. Type I corresponds to two-phase CO_2 -rich inclusions (H_2O_L and CO_{2L+V}); Type II corresponds to multiphase solid, CO_2 -rich inclusions (H_2O_L and CO_{2L+V}) with halite (H) and sometimes sylvite (S) daughter minerals.



Fig. 6. Histograms showing the degree of filling (DF) of the fluid inclusions at room temperature (A), and the decrepitation temperatures (T_D) for Types-I and -II fluid inclusions (B).



Fig. 7. SEM images of Type-II fluid inclusion cavities in quartz. (A) The cavity shows a salt identified as halite (NaCl) and a iron-rich daughter mineral (Fe). (B) The cavity presents crystals of calcite (Ca) trapped as solid inclusions and a salt identified as sylvite (KCl). q corresponds to a fragment of quartz which fell into the fluid inclusion cavity during it opening.

defined: Subtype IIA with 5 < DF < 40% and Subtype IIB with 55 < DF < 75% (Fig. 6A). The morphology of the solids (daughter phases) in the cavities and the qualitative chemical analysis obtained with the SEM, allow the identification of salts as halite, sylvite and other phases, as iron-rich oxydes or hydroxydes (Figs. 7A, B). Accidental trapped crystals of muscovite and calcite were also identified (Fig. 7B). Sylvite is not always present as a daughter mineral; halite is dominant.

The two FI types have irregular to negative crystal shape and are 8-25 μ m in size. Some Type-I FI reach 30 μ m. Transmitted light microscopy shows that the two types occur in the same areas of quartz plates (Fig. 5). They are usually found in close spatial association, either in mature fractures which do not cut the quartz grain boundaries, or widespread as clusters within deformation-free quartz domains. Furthermore, the observed inclusions which display a wide range of DF, do not show any visible evidence of necking-down or leakage. The relative proportions of each subtype vary from sample to sample, but are always associated in a single fracture or quartz grain. Therefore, the model invoking post-entrapment FI alterations is unlikely; especially, the hypothesis that subtype-B fluid inclusions would result from leakage of subtype-A fluid inclusions. The straight association of the two types of FI as clusters within quartz domains free of deformation or recrystallisation, and the presence of fluid inclusions which display variable degrees of infilling without evidence of post-entrapment alterations are criteria for the interpretation of inclusions as coeval and trapped at the same time.

Quartz is sometimes observed as solid inclusions in pyrite crystals deposited prior to or contemporaneous with pyrite growth. Thus, the two coeval types of FI will represent the best and unique record of the composition and evolution of the fluid phases responsible for transport and deposition of gold.

Results of microthermometric and Raman analysis

Type-I fluid inclusions

For all FI of Type I, T_{mCO_2} (final melting of solid CO₂) are in the range of $-62^{\circ}C/$ -56.6 °C, indicating the presence of other components than CO_2 in the volatile phase (Swanenberg, 1979). This is consistent with the variations observed for $T_{\rm mC}$ (melting temperature of clathrate), which are in the range of $+1^{\circ}C/+16^{\circ}C$ range (Figs. 8A, B). In some inclusions, we were able to observe the formation of a liquid in the remaining vapour after CO_2 freezing at temperatures between -170° and -180° C. The homogenization occurs to liquid at temperatures around -147°C, indicating that the liquid is N_2 . Eutectic melting temperatures (appearance of the first liquid droplet in ice) cluster around -23.0° C, close to the eutectic for the system H₂O-NaCl-KCl (Crawford, 1981). The salinities are variable, with ice final melting temperatures (T_{mI}) between -3.7° and -11.3° C for FI of subtype IA and between -7.5° and -11.6° C for FI of subtype IB.

During heating, the CO₂ phase homogenizes (T_{hCO_2}) to the vapor (IA_v, IB_v) or liquid (IA_l, IB_l) phase. The CO₂ homogenization temperature histogram (Fig. 8C) reveals an important scattering of T_{hCO_2} for FI of Type I. Subtype IA homogenizes to liquid or vapor with T_{hCO_2} between -20.9° and $+25^{\circ}$ C, and subtype IB homogenizes to liquid between -30° and $+5^{\circ}$ C. Decrepitation occurs in all inclusions at temperatures between 200° and 300°C (Fig. 6B). In subtype IA, the volume decrease of the vapor before reaching the temperature of decrepitation implies a probable total homogenization to liquid.

The Raman spectrometry results confirm the presence of non-CO₂ components in the volatiles. Beside CO₂ (the dominant species), N₂ and CH₄ are found in variable amounts, up to 35 mole% and <4 mole%, respectively (Table 2). In some Type-IA inclusions, no volatile



Fig. 8.(A). Histograms of CO₂ final melting temperature (T_{mCO_2}) ; (B) clathrate final melting temperature (T_{mC}) ; (C) CO₂-homogenization temperature (T_{HCO_2}) ; and (D) final dissolution temperatures of halite (T_{sNaCl}) and sylvite (T_{sKCl}) for Types-I and -II fluid inclusions. Same symbols as in Fig. 6.

component could be detected, although microthermometry data suggest the presence of volatiles in the vapour ($T_{mCO_2} = -57.0$, Table 2). This behaviour indicates the probable lowdensity of the volatile components. Raman data show also that FI of Type IB are signifi-

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TABLE 2

Туре	Size (µm)	DF (%)	$T_{\rm mCO_2}$	T _{mH2O}	<i>T</i> _{mC} (°C)	T _{HCO2}	$T_{ m h}$	$T_{\mathbf{D}}$	X _{CO2}	X _{CH4} (% mol)	X _{N2}	d _{vapor} (g/cm ³)	NaCl (wt%)
IAv	20	15	-57.7	- 10.7	2.5	24.6	-	269	93.10	2.06	4.84	0.33*	12.63*
IAv	15	20	- 58.5	-9.6	7.5	-20.9		115	69.61	1.16	29.73	0.18°	11.83°
IAi	15	10	- 57.0	-10.4	2.9	?	206 ₁	216	100	-	-	?	12.10*
IA	15	5	- 56.9	-10.5	9.4	?	_	243	100	-	-	?	1.22*
IB	10	55	-60.7	-6.7	2.8	-30.1	_	222	61.02	4.08	34.90	0.35°	8.12°
IB_1	10	90	- 58.3	-11.6	?	-1.8	-	279	79.78	-	20.22	0.30°	14.09°

Microthermometric and Raman data for selected types IA and IB fluid inclusions

Microthermometry: DF=degree of filling of FI at room temperature; T_m =temperature of final melting of: CO₂ (CO₂), H₂O (ice), C (clathrate); T_h =temperature of homogenization of: CO₂ (l: liquid; v: vapor; i: not seen), or total homogenization (one data in the liquid at 206°C); T_D =temperature of decrepitation; d_{vapor} =carbonic-phase density (g/cm³) calculated in (*) the CO₂ system (Parry, 1986) and in (°) the CO₂-N₂ system (Darimont and Heyen, 1988); NaCl (wt%)=salinity calculated with T_{me} (*) and T_{mH_2O} (°).

Raman data in mole% for CO₂, CH₄, N₂.

cantly richer in non-CO₂ components than Type IA.

Type-II fluid inclusions

The microthermometric data are summarized in Table 3. In some FI of Type II, liquid N_2 is present at low temperature $(T < -170^{\circ}C)$ around the carbonic vapour phase. It homogenizes to liquid at temperatures around $-148^{\circ}C$. The presence of an important concentration of N_2 is confirmed by Raman analysis (N₂ up to 48 mole%). For all FI of Type II, T_{mCO_2} ranges from -60.5° to -57.1° C; T_{mC} ranges from $+2.0^{\circ}$ to $+16.0^{\circ}$ C (Figs. 8A, B). T_{hCO_2} ranges from -15° to $+22^{\circ}$ C to liquid, and $+15^{\circ}$ to $+27^{\circ}$ C to vapour, respectively (Fig. 8C). Eutectic melting temperatures cluster around -25° C, close to the eutectic in the H₂O-NaCl-KCl system. Ice melting temperatures range from -9.6° to -20° C and hydrohalite melting temperatures up to $+2^{\circ}$ C.

The histograms of the dissolution tempera-

TABLE 3

Microthermometric and Raman data for selected types IIA and IIB fluid inclusions

Туре	Size (μm)	DF (%)	T_{mCO_2}	$T_{\rm HCO_2}$	T _{sNaCl} (°C)	$T_{\rm sKCl}$	$T_{\rm D}$	X _{CO2}	X _{CH₄} (% mol)	X _{N2}	d _{vapor} (g/cm ³)
IIA ₁ *	20	25	- 58.2	7.7	> 269	211	269	80.11	_	19.89	0.24
IIA	15	5	- 58.3	-15.1	>115		115	53.39	1.91	44.70	0.10
IIA ₁ *	20	15	- 57.5	18.7	281	239	281	75.25	5.16	19.59	0.15
IIA,*	15	10	- 57.9	20.5	>115	<u> </u>	115	79.37	0.97	19.66	0.20
IIA	10	10	- 57.8	21.0	>115	-	115	87.11	0.40	12.49	0.35
IIA;*	15	5	- 58.8	?	>247	169	247	69.00	1.04	29.96	0.21
IIB	10	55	- 58.6	- 8.0	>240	_	240	61.22	_	38.78	0.15
IIB ₁	15	75	- 58.5	-4.7	>218	-	218	51.75	-	48.25	0.10

*with sylvite daughter crystal.

Same captions as for Table 2.

 T_{sNaCl} and T_{sKCl} =temperature of final melting of halite and sylvite, respectively; the inclusion IIA₁ with T_{sNaCl} =281°C and T_{sKCl} =239°C indicates a salinity of 22 wt% eq. NaCl and 34 wt% eq. KCl, respectively. The carbonic-phase density was calculated in the the CO₂-N₂ system (Darimont and Heyen, 1988).

ture of halite and sylvite (Fig. 8D) show scattered values: T_s NaCl is widespread between 130°-290°C and T_s KCl between 60° and 240°C. Total homogenization was not measured due to decrepitation which generally occurred before the dissolution of the daughter phases. The range of decrepitation temperatures for FI of Type II are the same as for FI of Type I (Fig. 6B).

Identification of fluid phases and significance of the fluids trapped in the inclusions

The FI study led to the identification of two types of fluids: -(a) a highly saline H₂O-CO₂-bearing fluid with halite and/or sylvite daughter minerals, and (b) an H₂O-CO₂-bearing fluid with moderate salinities.

The two types of fluids are contemporaneous and display a notable variation in the degree of filling and dispersion of the microthermometric parameters. A CO₂-CH₄-N₂ triangular plot (Fig. 9) illustrates the chemical variation of the composition of the gas phase in the FI. This can be explained by a variable mixing of CO2 and N2 between two end-members, with CO_2/N_2 molar ratio up to 1. It reflects the mixing of CO_2 and N_2 with notable higher volatile concentrations in FI of Types IB or IIB and a decrease in N_2 for FI of Types IA or IIA. The T_{mCO_2} - T_{hCO_2} diagram (Fig. 10) shows an apparent decrease in CO₂-density as shown by the increase of T_{hCO_2} and the increase of T_{mCO_2} for Types IB₁ to IA₁ and IA_v, or for Types IIB₁ to IIA₁ and IIA₂. However, Raman microprobe spectrometry has revealed the high amount of N_2 (up to 50%) in these fluids and, thus, the CO₂-density of the non-aqueous part of the inclusions has to be considered using the phase equilibria conditions of the CO_2 - N_2 system (Darimont and Heyen, 1988). The corresponding densities (Tables 2 and 3) indicate rather higher carbonic-density in Types IA and IB $(0.2 < d_v < 0.35 \text{ g/cm}^3)$ than in Types IIA $(0.1 < d_v < 0.35 \text{ g/cm}^3)$ and IIB $(0.1 < d_v < 0.15 \text{ g/cm}^3).$

The bulk chemical composition and density of FI of Type I can be calculated using the method proposed by Ramboz (1980), but bulk V-X properties for FI of Type II cannot be obtained for NaCl-KCl-saturated CO₂-N₂-bearing brines. However, without thermodynamic data for such a chemical system, a crude estimation of the salinity of sylvite-free-bearing FI was calculated using the halite dissolution temperature (Hall et al., 1988); it corresponded to a salinity between 30 and 37 wt% eq. NaCl. The salinity of the sylvite-halitebearing FI, when the inclusion did not decrepitate before halite disappearance, was determined using the ternary NaCl-KCl-H₂O system (Sterner et al., 1988). It corresponded to about 22 wt% eq. NaCl and 34 wt% eq. KCl (Table 3). NaCl is by far the most dominant solute in the fluid. However, the presence of sylvite reveals the presence of large concentrations of KCl. For inclusions with $T_{\rm sKCl}$ > +170°C (Fig. 8D and Table 3), the brines are KCl dominated. If the remaining quantity of H_2O vapor was significant at the time of sylvite dissolution, the $T_{\rm sKCl}$ would be overestimated (Sterner et al., 1988). Considering the degree of filling (55 < DF < 75%) and the mode of homogenization of this type of FI, the calculated salinities in wt% eq. KCl are probably overestimated. Besides, the presence of appreciable amounts of CO_2 and N_2 in the liquid phase can significantly alter the phase relations of the NaCl-KCl-H₂O system, provoking particularly an overestimation of the NaCl and KCl contents for the concentrated brines.

Considering that both salt and dissolved CO₂ have a depressing effect on the H₂O activity, the ice-melting temperatures of FI of Type I suggest minimal salinities between 3.7 and 13.8 wt% eq. NaCl for Subtype IA, and between 9.2 and 14.0 wt% eq. NaCl for Subtype IB (Potter et al., 1978). In such N₂-bearing fluids, it is impossible to estimate the salt concentration from $T_{\rm mC}$ using data of the H₂O-NaCl-CO₂ system as reported by Collins (1979). How-



Fig. 9. CO_2 - CH_4 - N_2 diagram of Types-I and -II fluid inclusions showing the chemical variation in composition of the gas phase (Raman analyses) materialized by variable mixtures of CO_2 and N_2 . *IAv* or *IIAv*=fluid inclusion of which CO_2 -phase homogenizes in the vapor; *IBl* or *IIBl*=fluid inclusion of which CO_2 -phase homogenizes in the liquid; *IAi* or *IIAi*=fluid inclusion of which CO_2 phase homogenizes in the liquid; *IAi* or *IIAi*=fluid inclusion of which CO_2 phase homogenizes in the liquid; *IAi* or *IIAi*=fluid inclusion of which CO_2 phase homogenizes in the liquid; *IAi* or *IIAi*=fluid inclusion of which CO_2 phase homogenizes in the liquid; *IAi* or *IIAi*=fluid inclusion of which CO_2 phase homogenizes in the liquid; *IAi* or *IIAi*=fluid inclusion of which CO_2 phase homogenizes in the liquid; *IAi* or *IIAi*=fluid inclusion of which CO_2 phase homogenizes in the liquid; *IAi* or *IIAi*=fluid inclusion of which CO_2 phase homogenizes in the liquid; *IAi* or *IIAi*=fluid inclusion of which CO_2 phase homogenizes in the liquid; *IAi* or *IIAi*=fluid inclusion of which CO_2 phase homogenizes in the liquid; *IAi* or *IIAi*=fluid inclusion of which CO_2 phase homogenizes in the liquid; *IAi* or *IIAi*=fluid inclusion of which CO_2 phase homogenizes homogenizes in the liquid; *IAi* or *IIAi*=fluid inclusion of which CO_2 phase homogenizes hom



Fig. 10. T_{mCO_2} versus T_{HCO_2} (°C) diagram for Types-I and -II fluid inclusions. L= homogenization of the CO₂ phase in the liquid; V= homogenization in the vapor.

ever, for some N₂-CH₄-free FI of type IA (Table 2), $T_{\rm mC}$ give salinities between 1 and 12 wt% eq. NaCl, which are in the range of the minimal values defined by $T_{\rm mi}$ (Table 2) for all FI of Type I.

The distribution and chronology of the fluid inclusions in quartz showed that the fluids were trapped simultaneously. This coexistence rules out the possibility of trapping different fluids at different times. The simultaneous trapping of fluids with variable compositions in the system $H_2O-CO_2-N_2-NaCl-KCl$, evident by the presence of mixed inclusion assemblages (FI of Types I and II), raises the question about the processes involved for such an association of FI.

Three possibilities are considered:

(1) Unmixing from an homogeneous H_2O_{-} CO₂-N₂-NaCl-KCl fluid resulting in the cogeneration of two fluids with contrasted density and composition: a high-density saline brine poor in CO₂-N₂ volatiles, and a low-salinity and low-density CO₂-N₂-rich vapour (Ramboz et al., 1982). As a consequence of unmixing, the two types of FI must homogenize to the liquid and to the vapour, respectively, at the same temperature. On heating, the two types of inclusions must have the same behaviour concerning decrepitation. This mechanism of unmixing is frequently described in metamorphic environments (e.g., Trommsdorff et al., 1985; Craw, 1988). Bowers and Helgeson (1983) and Skippen and Trommsdorf (1986) have discussed non-ideal mixing in the system H_2O-CO_2 -NaCl at high P-T in metamorphosed-carbonate rocks. Fluid unmixing is also proposed to be responsible for metal deposition in some gold deposits (Robert and Kelly, 1987; Williams-Jones and Ferreira, 1989) or tin deposits (Ramboz, 1980). The FI in the Santa Rita gold deposit are contemporaneous and their decrepitation temperatures are in the same range. However, they contain variable mixtures of H₂O-carbonic-NaCl and KCl components: FI of Type II is carbonic-rich and FI of Type I shows low to moderate salinities with notably higher values for the carbonic-rich Subtype IB. Moreover, the two end-member fluid compositions (expected in the case of unmixing mechanism of a parent homogeneous fluid) are not found in FI in Santa Rita. As a consequence, this mechanism cannot account for the coexistence of the observed fluids.

(2) FI of Types I and II are the result of necking-down or decrepitation FI alteration process, as described in HT-HP metamorphic environments (Hollister et al., 1979) or in synthetic FI experiments (Pêcher and Boullier, 1984; Bakker and Jansen, 1991). In the case of Santa Rita, leakage or necking-down is not a common feature, as indicated in the fluid inclusion description and this model has been already abandoned from the observation of FI.

(3) A mechanism of heterogeneous trapping. Entrapment of fluids with variable compositions (in the $H_2O-CO_2-N_2-NaCl-KCl$ system) in the same inclusion may be the result of the mixing of two different fluids: a high-salinity fluid ($H_2O-NaCl-KCl$ system) and a carbonic fluid ($H_2O-CO_2-N_2$ system). The mechanism of heterogeneous trapping implies that the fluids were contemporaneous and suggests a fluid immiscibility process (Roedder and Bodnar, 1980; Ramboz et al., 1982; Roedder, 1984; Touret, 1987).

This genetic model is preferred considering that the fluid inclusions observed in the Santa Rita quartz veins are in agreement with the criteria defined for heterogeneous trapping (Ramboz et al., 1982), i.e., simultaneous trapping of all the fluid inclusions assemblage; absence of leakage or necking-down; and a wide range of degree of filling and of compositions in the fluid inclusions.

Heterogeneous trapping invalidates the use of the homogenization temperature for geologic thermometry, particularly as the $T_{\rm h}$ are always shifted towards higher values (Ramboz et al., 1982). In Santa Rita, all the inclusions decrepitate before total homogenization in the range 200°-300°C; the accurate temperature of trapping remains unknown.

Such heterogeneous trapping of two separate fluids has already been reported for other CO_2 -brine-high salinity systems, for example in quartz veins from the Coronation mine (Arnold and Rutherford, 1969), in uranium deposits (Fuzikawa, 1982), in the Himalayan crustal shear-zone (Pêcher, 1979), or, more recently, in the generation of gold mineralization in the Transvaal carbonated sequences (Anderson et al., 1992).

Possible origin of the fluids and associated brines

Occurrences of gold in the Niquelandia district are distributed in areas where the carbonate-psammitic and pelitic sequences have been metamorphosed up to greenschist facies (biotite zone).

The compositions of FI in quartz from the Santa Rita veins and veinlets show that the fluids were rich in CO_2-N_2 and dissolved salts at the time of trapping. It is difficult to assess if the fluids were trapped during the peak of the metamorphism, but the development of a hydrothermal system had to be related to the persistance of an abnormally high thermal gradient. There is no evidence of igneous activity in the region and an orthomagmatic or possible mixed meteoric-orthomagmatic fluids origin is discounted.

A high regional heat flow would provoke the production of notable quantities of CO_2 which mixed with the circulating fluids by heating the dolomite-limestone levels of the Paranoá sequences. These devolatilization reactions should result also in the liberation of important quantities of N_2 by the reduction of N_2 from NH⁴⁺ present in mica and feldspar lattices (Duit et al., 1986). The Paranoá carbonaceous phyllites would be a good candidate for such NH⁴⁺ bearing rocks.

A metamorphic origin of CO_2 and N_2 appears reasonable, however, the source of the

fluid is a problem: metamorphic, meteoric, mixed or other?

In the case of a metamorphic contribution, the devolatilization process of carbonate rocks would produce a large quantity of CO_2 at low water-rock ratios.

The presence of meteoric fluids in the Santa Rita hydrothermal system cannot be proved by FI study, but can be discussed following the example of the Southern Alps in New Zealand near major fault zones (Craw and Koons, 1989) where gold mineralization is dissociated to heat flow circulations and mixing of metamorphic and meteoritic fluids. The proposed model, relating to shallow conductive thermal anomalies along fault zones with moderate uplift rates (Craw and Koons, 1989) is convincing and can perhaps be extended, as proposed by the authors, to the Archaean and Proterozoic where higher geothermal gradients prevailed. In fact, the Paranoá gold mineralizations are structurally controlled by faults and fractures resulting from the reactivation of older regional lineaments (i.e., the Niquelandia-Campos Belos and Minacu-Cana Brava lineaments; see Fig. 2). High geothermal gradients probably prevailed locally in these Proterozoic fault zones and might be responsible for the Paranoá hydrothermal fluid circulations.

In consequence, the model of a Proterozoic geothermal system involving a regional thermal gradient can be proposed for the Paranoá gold occurrences. This gradient remained high in the interior of the belt and slowly decreased following the compressive phases of the Brasiliano Cycle (Olivo and Marini, 1988).

Other nonmetamorphic sources for the brines can be inferred, including probable leaching by fluids from thick evaporitic beds which occur in the lower part of the Paranoá lithostratigraphic column (Fig. 3). As in recent hydrothermal systems, the chemical composition of the fluids is derived by leaching of rock through a continuous water flow (Mc Kibben and Williams, 1989). In sedimentary basins, the dissolution of evaporites may result in an atypical composition of the fluids as in the highly mineralized brines of the Salton Sea geothermal system (Mc Kibben et al., 1988). The dissolution of marine halite levels rich in anhydrite (Dubessy and Ramboz, 1986) would be the result of oxidation of organic NH⁴⁺ and CH₄ reacting with sulfates, leading to the production of CO₂ coexisting with N₂ and a notable enrichment of H₂S in the resulting fluid. Such a CO₂-N₂ hypersaline composition is also found in the Santa Rita brines. Thus, considering the geological and fluid inclusions evidence, the evaporitic origin for the Santa Rita brines is highly probable.

Implications for gold transport and deposition

In Santa Rita, primary gold ore is related to pyrite-bearing quartz-carbonate veins. Native gold is unknown in this deposit and fire assay determinations indicate that pyrite remains the sole potential gold-bearing sulphide. Milky quartz is sometimes observed as solid inclusions in pyrite crystals and its precipitation is prior to or contemporaneous with pyrite crystallization. The fluid inclusion study demonstrated the presence of mixed assemblages with variable degrees of filling and range of density indicating the heterogeneous trapping of two fluids between 200° and 300°C. The mixing of these fluids would be an important factor for pyrite deposition.

As-Co-Ni enrichments in the hydrothermally altered wallrocks of the veins (Olivo, 1989) and in the pyrites illustrate that the oreforming fluids were enriched in these elements, and supersaturated with respect to FeAsS composition. Under these conditions, the absence of arsenopyrite in the veins implies that the f_{S_2} was high.

The origin of the gold is unknown but was probably transported by the same As-Co-Nirich-bearing hydrothermal fluids. Gold solubility in crustal systems is a function of salinity, CO_2 content and temperature of the fluids. If the gold transport for the Santa Rita deposit is related to the fluids trapped by the milky quartz, the CO₂-rich hypersaline brines may have played a predominant role (Berger and Henley, 1989). Following this hypothesis, gold was probably transported as $AuCl_2^-$ complex ($T > 300^{\circ}C$, low pH, moderate f_{O2} -pyrite field stability). As temperature decreased and mixing of the fluids proceeded below 290°C, the CO_2/H_2S ratio of the fluid decreased, and the "switch over" process described by Large et al. (1989) would lead to a predominance of $Au(HS)_2^-$ in the fluid. Gold-bearing pyrite would precipitate in this interval of low temperatures.

The low-T conditions of the Santa Rita gold mineralization and mixing of fluids are also indicated by the As-Co-Ni-bearing pyrites. The As-oscillatory zonings observed in the Santa Rita pyrite were already described in other gold deposits from various geological environments (Fleet et al., 1989; Mac Lean and Fleet, 1989), in active geothermal systems (Ballantyne and Moore, 1988) and in stratabound and stratiform Carlin gold-type deposits (Wells and Mullins, 1973).

These As-oscillatory zonings indicate variations in fluid composition during pyrite growth. Fleet et al. (1989) correlated these zonings to episodic fluid pulses in low-temperature hydrothermal systems. Such changes in fluid composition can be favoured by a mechanism of fluid mixing but not by the simple cooling of an homogeneous fluid. The proposed mechanism of the heterogeneous trapping of two separate fluids in the system H₂O-CO₂-N₂-NaCl-KCl, and the resulting changes in the physicochemical conditions caused by the fluid mixing is a conspicuous process for the Santa Rita hydrothermal fluid evolution. Moreover, the different geometry and the broad As-Co growth bandings of pyrite (Fig. 4), cannot be explained by a repeated and regular recharge and precipitation of As and Co in an overall equilibrium fluid. The hypothesis of intermittent supplies and changes in fluid composition with variable As and Co contents is most likely. Following this hypothesis, the fluid composition entering the area of mineralization was closely related to the amount of inflow of highly saline fluid. The supply of brine has probably decreased progressively in time due to decreasing of the regional thermal gradient and the consequent closing of the hydrothermal system.

The proposed model of a Proterozoic geothermal system characterized by a heat fluid flow regime along fault structures which crosscut the Paranoá evaporites, implies that $H_2O CO_2-N_2-NaCl-KCl$ hypersaline fluids might be expected in the mineralized quartz structures of other Paranoá Group gold deposits.

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References

- Almeida, F.F.M., Hasui, Y., Neves, B.B.B. and Fuck, R.A., 1977. Províncias estruturais brasileiras. VIII Simp. Geol. Nordeste, Recife, 8: 363–391.
- Anderson, M.R., Rankin, A.H. and Spiro, B., 1992. Fluid mixing in the generation of mesothermal gold mineralization in the Transvaal sequence, Transvaal, South Africa. Eur. J. Mineral., 4: 933–948.
- Angeiras, A.G., Costa, L.A.M. and Santos, R.C., 1988. Deposito de ouro de Mara Rosa, Goiás. In: C. Schobbenhaus and C.E.S. Coelho (Editors), Principais Depósitos Minerais do Brasil. DNPM, Brasilía, 3: 523-534.
- Arnold, R.G. and Rutherford, M.J., 1969. Data for brine and carbon dioxide filled liquid inclusions in quartz veins from the Coronation Mine. Geol. Surv. Can., Pap. 68(5): 213–228.
- Ballantyne, J.M. and Moore, J.N., 1988. Arsenic geochemistry in geothermal systems. Geochim. Cosmochim. Acta, 52: 475–483.
- Bakker, R.J. and Jansen, J.B.H., 1991. Experimental postentrapment water loss from synthetic inclusions in

natural quartz. Geochim. Cosmochim. Acta, 55: 2215-2230.

- Berger, B.R. and Henley, R.W., 1989. Advances in the understanding of epithermal gold-silver deposits, with special reference to the western United States. Econ. Geol., Mongr. 6: 405–423.
- Boiron, M.C., Cathelineau, M., Dubessy, J. and Bastoul, A.M., 1990. Fluids in Hercynian Au veins from the French Variscan belt. Mineral. Mag., 54: 231-243.
- Bowers, T.S. and Helgeson, H.C., 1983. Calculation of the thermodynamic consequences of non-ideal mixing in the system H₂O-CO₂-NaCl on phase relations in geologic systems: metamorphic equilibria at high pressures and temperatures. Am. Mineral., 68: 1059–1075.
- Collins, P.L.F., 1979. Gas hydrates in CO_2 -bearing fluid inclusions and the use of freezing data for estimation of salinity. Econ. Geol., 74: 1435–1444.
- Craw, D., 1988. Shallow-level metamorphic fluids in a high uplift rate metamorphic belt; Alpine schist, New Zealand. J. Metamorph. Geol., 6: 1–16.
- Craw, D. and Koons, P.O., 1989 Tectonically induced hydrothermal activity and gold mineralization adjacent to major fault zones. Econ. Geol., Mon. 6: 471-478.
- Crawford, M.L., 1981. Phase equilibria in aqueous fluid inclusions. In: L.S. Hollister and M.L. Crawford (Editors), Short Course in Fluid Inclusions. Applications to Petrology. Mineral. Assoc. Can., Vol. 6: 75–100.
- Danni, J.C.M., 1988. Os greenstone belts da Província Tocantins no Estado de Goiás, Brazil. Rev. Bras. Geosci., 18(4): 381-390.
- Dardenne, M.A. and Faria, A., 1985. Estratigrafia do Grupo Paranoá na região de Alto Paraiso, Goiás. 2nd Simp. Geologia do Centro-Oeste, Goiânia, Ata, pp. 65– 71.
- Darimont, A. and Heyen, G., 1988. Simulation des équilibres de phases dans le système CO₂-N₂. Applications aux inclusions fluides. Bull. Mineral., 111: 179-182.
- Dubessy, J. and Ramboz, C., 1986. The history of organic nitrogen from early diagenesis to amphibolite facies: mineralogical, chemical, mechanical and isotopic consequences. Vth Int. Symp. Water-Rock Interaction, Reykjavik, Iceland. Ext. Abstr., pp. 171–174.
- Duit, W., Jansen, J.B.H., Breemen, A.V. and Bos, A., 1986. Ammonium micas in metamorphic rocks as exemplified by Dome de l'Agout (France). Am. J. Sci., 286: 702-732.
- Fleet, M.E., Mac Lean, P.J. and Barbier, J., 1989. Oscillatory-zoned As-bearing pyrite from stratabound and stratiform gold deposits: an indicator of ore fluid evolution. Econ. Geol., Monogr. 6: 356–362.
- Fortes, P.T.F.O. and Nilson, A.A., 1990. Geologia dos corpos de minério do depósito de ouro Mina III, Crixás, Goiás. Bol. Resumo XXXVI Congr. Bras. Geol., Natal, pp. 146–147.
- Fortes, P.T.F.O. and Giuliani, G., 1992. Estudo preliminar dos fluidos associados aos corpos de sulfeto ma-

ciço do déposito aurífero Mina III, Crixás, Goiás. Soc. Bras. Geol. Nucleo Centro-Oeste, Bol., 15: 99-109.

- Fuzikawa, K., 1982. Fluid inclusion and oxygen isotope studies of the Nabarlek uranium deposit, Australia. Ph.D. thesis, Univ. Adelaide, 226 pp.
- Giuliani, G., Fortes, P.T.F.O., Olivo, G.R., Ronchi, L.H., Santos, M.M., Dardenne, M.A., Marini, O.J. and Nilson, A.A., 1991a. Contrasting Archean-Proterozoichosted gold deposit types ans associated gold-bearing fluids. In: M. Pagel and J. Leroy (Editors), Transport, Source and Deposition of Metals. Balkema, Rotterdam, pp. 665-668.
- Giuliani, G., Olivo, G.R., Marini, O.J., Dubessy, J. and Michel, D., 1991b. CO₂-N₂ hypersaline-bearing fluids associated to the Santa Rita hydrothermal gold occurrences, Paranoá group, Goiás, Brazil. Plinius, 5: 91– 92.
- Guha, J., Huan-Zhang Lu, Benoît Dubé, Robert, F. and Gagnon, M., 1991. Fluid characteristics of vein and altered wall-rock in Archean mesothermal gold deposits. Econ. Geol., 86: 667–684.
- Haggemann, S., Leonardos, O.H., Walde, D.H.G. and Rodrigues Neto, L., 1988. The gold-bearing Canastra phyllites of Luzânia: a model of thin skinned thrust mineralization in the Brasília Belt. Ext. Abstr. Gold'88, Melbourne, Vol. 1: 187–189.
- Haggemann, S., P.E. Brown and D.H.G. Walde, 1992. Thin-skinned thrust mineralization in the Brasília fold belt: the example of the old Luziânia gold deposit. Mineral. Deposita, 27(4): 293-303.
- Hall, D.L., Sterner, S.M. and Bodnar, J., 1988. Freezing point depression of NaCl-KCl-H₂O solutions. Econ. Geol., 83: 197-202.
- Ho, S.E., Robert, F. and Groves, D.I., 1990. Gold and base-metal mineralization in the Abitibi subprovince, Canada, with emphasis on the Quebec segment. Short Course Notes, Univ. Western Australia, 24, 273 pp.
- Hollister, L.S., Burruss, R.C., Henry, D.L. and Hendel, E.M., 1979. Physical conditions during uplift of metamorphic terranes, as recorded by fluid inclusions. Bull. Mineral., 102: 555–561.
- Keays, R.R. and Skinner, B.J., 1989. Introduction. In: R.R.
 Keays, W.R.H. Ramsay and D.I. Groves (Editors), The Geology of Gold deposits: The Perspective in 1988.
 Econ. Geol., Monogr. 6: 1-8.
- Kishida, A., Lobato, L., Lindenmeyer, Z. and Fyfe, W.S., 1990. Introduction: Brazil, the sleeping ressource giant.
 In: A Group of Papers devoted to Mineral Deposits of Brazil. Econ. Geol., 5: 899–903.
- Kuyumjian, R.M. and Dardenne, M.A., 1983. O controle das mineralizaçães auríferas do greenstone belt da faixa Crixás (Goiás). Simp. Sobre Mineralizaçães Auríferas no Estado da Bahia, Anais, pp. 56–59.
- Lacerda, H., 1986. Tipologia das mineralizaçães auríferas da área do Rio do Carmo, Cavalcante, Goiás. XXXIV Congr. Bras. Geol., Goiânia, 5: 1946–1955.

- Lacerda, H., 1991. Gold in Central Brazil: types of deposits, their economic significance and regional distribution. In: E.A. Ladeira (Editor), Brazil Gold'91, pp. 195-202.
- Lacerda, H. and Pereira, A.A., 1988. Contribuição a tipologia das mineralizações auríferas prímarias da região de Uruaçú-Niquelândia, Goiás. XXXV Congr. Bras. Geol., Belém, 1: 107–115.
- Large, R.R., Huston, D.L., McGoldrick, P.J. and Ruxton, P.A., 1989. Gold distribution and genesis in Australian volcanogenic massive sulfide deposits and their significance for gold transport models. Econ. Geol., Monogr. 6: 520-535.
- Leonardos, O.H., Jost, H. and Veiga, A.T.C., 1988. Brazilian gold districts: how many are not associated with shear zones? Ext. Abstr. Gold'88, Melbourne, pp. 611– 613.
- Leonardos, O.H., Jost, H. and Oliveira, C.G., 1991. Gold deposits and shear zone relationships in the Precambrian of Brazil. In: E.A. Ladeira (Editor), Brazil Gold'91, pp. 167–169.
- Mac Lean, P.J. and Fleet, M.E., 1989. Detrital pyrite in the Witwatersrand gold fields of South Africa: evidence from truncated growth banding. Econ. Geol., 84: 2008–2011.
- Magalhães, L.F., Lobo, R.L.M., Botelho, L.C.A. and Pereira, R.C., 1988. Depósito de ouro de Meia Pataca, Crixás, Goiás. In: C. Schobbenhaus and C.E.S. Coelho (Editors), Principais Depósitos Minerais do Brasil, Vol. 3: 499-522.
- Marini, O.J. and Botelho, N.F., 1986. A Província de granitos estaníferos de Goiás. Rev. Bras. Geoci., 16(1): 119–131.
- Marini, O.J. and Queiroz, E.T., 1991. Main geologic-metallogenetic environments and mineral exploration in Brazil. Ciênc. Cult., 43(2): 153–161.
- Marini, O.J., Fuck, R.A., Dardenne, M.A. and Danni, J.C.M., 1984. Província Tocantins: setores central e sudeste. In: F.F.M. Almeida and Y. Hasui (Editors), O Precambriano do Brasil E. Blücher, São Paulo, pp. 205-264.
- Marion, P., Monroy, M., Holliger, P., Boiron, M.C., Cathelineau, M., Wagner, F.E. and Friedl, J., 1991. Gold-bearing pyrites: a combined ion microprobe and Mössbauer spectrometry approach. In: M. Pagel and J. Leroy (Editors), Source, Transport and Deposition of Metals. Balkema, Rotterdam, pp. 677–680.
- Mc Kibben, M.A. and Williams, A.E., 1989. Metal speciation and solubility in saline hydrothermal fluids: an empirical approach based on geothermal brine data. Econ. Geol., 84: 1996–2007.
- Mc Kibben, M.A., Williams, A.E. and Okubo, S., 1988. Metamorphosed Plio-Pleistocene evaporites and the origins of hypersaline brines in the Salton Sea geothermal system, california: fluid inclusion evidence. Geochim. Cosmochim. Acta, 52: 1047–1056.

- Olivo, G.R., 1989. Controle litoestratigrafico e genese das ocorrencîas auríferas da sequência psamo-pelito-carbonatica do Grupo Paranoá, Goiás. M.Sc. thesis, Univ. Brasília, 296 pp.
- Olivo, G.R. and Marini, O.J., 1988. Ouro no Grupo Paranoá: distribuição, tipos e contróles das ocorrencîas. Congr. Bras. Geol., Belém, 35(1): 93-106.
- Parry, W.T., 1986. Estimation of XCO₂, P, and fluid inclusion volume from fluid inclusion temperature measurements in the system NaCl-CO₂-H₂O. Econ. Geol., 81: 1009-1013.
- Pêcher, A., 1979. Les inclusions fluides de quartz d'exsudation de la zone MCT himalayen au Népal central: données sur la phase fluide dans une grande zone de cisaillement crustal. Bull. Mineral., 102: 537–554.
- Pêcher, A. and Boullier, A.M., 1984. Evolution à pression et température élevées d'inclusions fluides dans un quartz synthétique. Bull. Minéral., 107: 139–153.
- Potter, R.W., Clynne, M.A. and Brown, D.L., 1978. Freezing point depression of aqueous sodium chloride solutions. Econ. Geol., 73: 284–285.
- Poty, B., Leroy, J. and Jachimowicz, L., 1976. Un nouvel appareil pour la mesure des températures sous le microscope: l'installation de microthermométrie "Chaixmeca". Bull. Soc. Fr. Minéral. Cristallogr., 99: 181–186.
- Pulz, G.M., Jost, H., Michel, D. and Giuliani, G., 1991a. The Archaean Maria Lázara gold deposit, Goiás, Brazil: example of Au-Bi-Te-S metallogeny related to shear zones intruded by synkinematic granitoids. In: E.A. Ladeira (Editor), Brazil Gold'91. Balkema, Rotterdam, pp. 385-387.
- Pulz, G.M., Giuliani, G., Jost, H. and Michel, D., 1991b. Maria Lázara gold deposit (Goiás state, Brazil): an example of intense fluid-rock interaction associated with a triple point structure. In: M. Pagel and J. Leroy (Editors), Source, Transport and Deposition of Metals. Balkema, Rotterdam, pp. 117–118.
- Ramboz, C., 1980. Géochimie et étude des phases fluides de gisements et indices d'étain-tungstène du sud du Massif Central, Ph.D thesis, University of Nancy, 278 pp.
- Ramboz, C., Pichavant, M. and Weisbrod, A., 1982. Fluid immiscibility in natural processes: use and misuse of fuid inclusion data. Chem. Geol., 37: 29–48.
- Richardson, S.V., Kesler, S.E. and Essene, E.J., 1986. Origin and geochemistry of the Chapada Cu-Au deposit, Goiás, Brazil: a metamorphosed wall-rock porphyry copper deposit. Econ. Geol., 81: 1884–1898.
- Robert, F. and Kelly, W.C., 1987. Ore-forming fluids in Archean gold-bearing quartz veins at the Sigma Mine, Abitibi greenstone belt, Quebec, Canada. Econ. Geol., 82: 1464–1482.
- Robert, F., Sheahan, P.A. and Green, S.B., 1990. Greenstone gold and crustal evolution. Nuna conference, Val

d'or, Québec, Geol. Assoc. Can., 252 pp.

- Roedder, E., 1984. Fluid inclusions. Mineral. Soc. Am., Rev. Mineral., 12, 646 pp.
- Roedder, E. and Bodnar, R.J., 1980. Geologic pressure determinations from fluid inclusion studies. Ann. Rev. Earth Planet. Sci., 8: 263–301.
- Romberger, S.B., 1986. The solution chemistry of gold applied to the origin of hydrothermal deposits; In: L.A. Clarck (Editor), Gold in the Western Shield, Montreal. Can. Inst. Min. Metall., Spec. Vol., 38: 168–186.
- Seward, T.M., 1973. Thiocomplexes of gold and the transport of gold in hydrothermal solutions. Geochim. Cosmochim. Acta, 37: 379–399.
- Shenberger, D.M. and Barnes, H.L., 1989. Solubility of gold in aqueous sulfide solutions from 150 to 350°C. Geochim. Cosmochim. Acta, 53: 269–278.
- Sibson, R.H., Robert, F. and Poulsen, K.H., 1988. Highangle reverse faults, fluid pressure cycling and mesothermal gold-quartz deposits. Geology, 16: 551–555.
- Skippen, G. and Trommsdorff, V., 1986. The influence of NaCl and KCl on phase relations in metamorphosed carbonate rocks. Am. J. Sci., 286: 81–104.
- Sterner, M.S., Hall, D.L. and Bodnar, R.J., 1988. Synthetic fluid inclusions. V. Solubility relations in the system NaCl-KCl-H₂O under vapor saturated conditions. Geochim. Cosmochim. Acta, 52: 989-1005.
- Swanenberg, H., 1979. Phase equilibria in carbonic system and their application to freezing studies of fluid inclusions. Contrib. Mineral. Petrol., 68: 303-306
- Thomson, M.L. and Fyfe, W.S., 1990. The Crixás gold deposit, Brazil: thrust-related, postpeak metamorphic gold mineralization of possible Brasiliano cycle age. Econ. Geol., 85: 928–942.
- Touret, J., 1987. Fluid inclusions and pressure-temperature estimates in deep-seated rocks. In: H.C. Helgeson (Editor), Chemical transport in Metasomatic Processes. Reidel, Dordrecht, pp. 91-121.
- Trommsdorff, V., Skippen, G. and Ulmer, P., 1985. Halite and sylvite as solid inclusions in high grade metamorphic rocks. Contrib. Mineral. Petrol., 89: 24–29.
- Wells, J.D. and Mullens, T.E., 1973. Gold-bearing arsenian pyrite determined by microprobe analysis, Cortez and Carlin gold mines, Nevada. Econ. Geol., 68: 187– 201.
- Williams-Jones, A.E. and Ferreira, D.R., 1989. Thermal metamorphism and H₂O-CO₂-NaCl immiscibility at Patapedia, Quebec: evidence from fluid inclusions. Contrib. Mineral. Petrol., 102: 247–254.
- Zini, A., Forlim, R., Andreazza, P. and Souza, A., 1988. Depósito de ouro do Morro do Ouro, Paracatu, Minas Gerais. In: C. Schobbenhaus and C.E.S. Coelho (Editors), Principais depósitos minerais do Brasil. DNPM, Brasília, 3: 479–489.