



# CHLORITE GEOTHERMOMETRY AND PHYSICO-CHEMICAL CONDITIONS OF GOLD MINERALIZATION IN THE PALEOPROTEROZOIC CAXIAS DEPOSIT, SÃO LUÍS CRATON, NORTHERN BRAZIL

E.L. Klein<sup>1</sup> & J.C. Koppe<sup>2</sup>

<sup>1</sup>CPRM/Geological Survey of Brazil, Av. Dr. Freitas, 3645, CEP 66095-110, Belém, PA

<sup>2</sup>Universidade Federal do Rio Grande do Sul, Av. Osvaldo Aranha, 99/504, CEP 00000-000, Porto Alegre, RS

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## ABSTRACT

*The Paleoproterozoic Caxias lode-gold deposit of São Luís Craton is hosted by a ductile-brittle shear zone crosscutting Caxias microtonalite (1982 ± 6 Ma). Microprobe analyses of hydrothermal chlorites were used to constrain formation temperature of chlorites and of the mineralization as a whole, along with P, pH,  $fO_2$  and  $fS_2$ . Among the empirical geothermometers, Zang & Fyfe (1995) showed to be the more efficient, due to compositional similarities between Caxias chlorites and those used in the calibration of the geothermometer, yielding a 262°-307°C temperature range. This temperature range, combined with previous fluid inclusion data and with mineral paragenesis, allowed P estimation between 1.6 and 3.7 kb;  $\log fO_2$  between -29.8 and -34.2;  $\log fS_2$  between -10 and -11; and a near neutral pH for the mineralizing fluid.*

## RESUMO

*O depósito aurífero filoneano Paleoproterozóico do Caxias, no Cráton São Luís, está hospedado em zona de cisalhamento dúctil-rúptil, que corta o microtonalito Caxias (1982 ± 6 Ma). Análises, por microsonda eletrônica, de cloritas associadas à mineralização foram utilizadas para determinação da temperatura de formação dessas cloritas e, por extensão, da temperatura de formação da mineralização, além de parâmetros como P, pH,  $fO_2$  e  $fS_2$ . Dentre os geotermômetros testados, o de Zang & Fyfe (1995) mostrou-se mais eficiente, devido às similaridades composicionais entre as cloritas do depósito do Caxias e as utilizadas na calibração desse geotermômetro, fornecendo temperaturas de formação entre 262° e 307°C. Estas temperaturas, juntamente com dados preexistentes de inclusões fluidas e de paragéneses minerais, permitiram estimativas de P entre 1,6 e 3,7 kb;  $\log fO_2$  entre -29,8 e -34,2;  $\log fS_2$  entre -10 e -11 e pH neutro para o fluido mineralizador.*

## INTRODUCTION

Chlorites are phyllosilicates largely distributed in several geological environments, occurring as products of ferromagnesian minerals substitution or precipitating directly from solutions. They form solid solutions and show variable degree of substitution. Especially, Al substitutes Si in tetrahedral sites and Mg substitutes Fe in octahedral sites, which makes chlorites chemical composition also variable. It is currently known that these variations are related to the bulk composition of the host rock, to increasing effects of metamorphism and to hydrothermal alteration, and that they record the physicochemical conditions of chlorite crystallization (Walshe, 1986; Cathelineau, 1988; Laird, 1988; Schiffman & Fridleifsson, 1991; De Caritat *et al.*, 1993; Walker, 1993; Zang & Fyfe, 1995; Xie *et al.*, 1997). Accordingly, and given that chlorites are commonly found in hydrothermal paragenesis, their non-stoichiometric characteristic has been widely used to place constraints on thermodynamic conditions of ore deposits formation (e.g., Kranidiotis & MacLean, 1987; Neall & Phillips, 1987; Kavalieris *et al.*, 1990; Zang & Fyfe, 1995; Lu *et al.*, 1996).

The Caxias gold deposit is one of the several examples of shear zone-hosted lode deposits and prospects occurring in São Luís Craton in northern Brazil (Fig. 1), having an unofficial production of more than 1 ton gold. The hosting shear zone crosscuts both schists (south-Caxias) and a hydrothermally-altered, fine-grained tonalite – the Caxias microtonalite (Klein, 1998; Klein *et al.*, 1999). This paper will deal with

the mineralizing conditions of the northern sector of the deposit (N-Caxias), therefore, on the mineralization hosted by Caxias microtonalite. Microprobe analyses of hydrothermal chlorites from the alteration zone, together with the knowledge of mineral paragenesis and previous fluid inclusion data on gold-related quartz veinlets (Klein *et al.*, 2000), are used to place constraints on T-P- $fO_2$ - $fS_2$ -pH of gold deposition in Caxias deposit.

## SAMPLING AND ANALYTICAL PROCEDURES

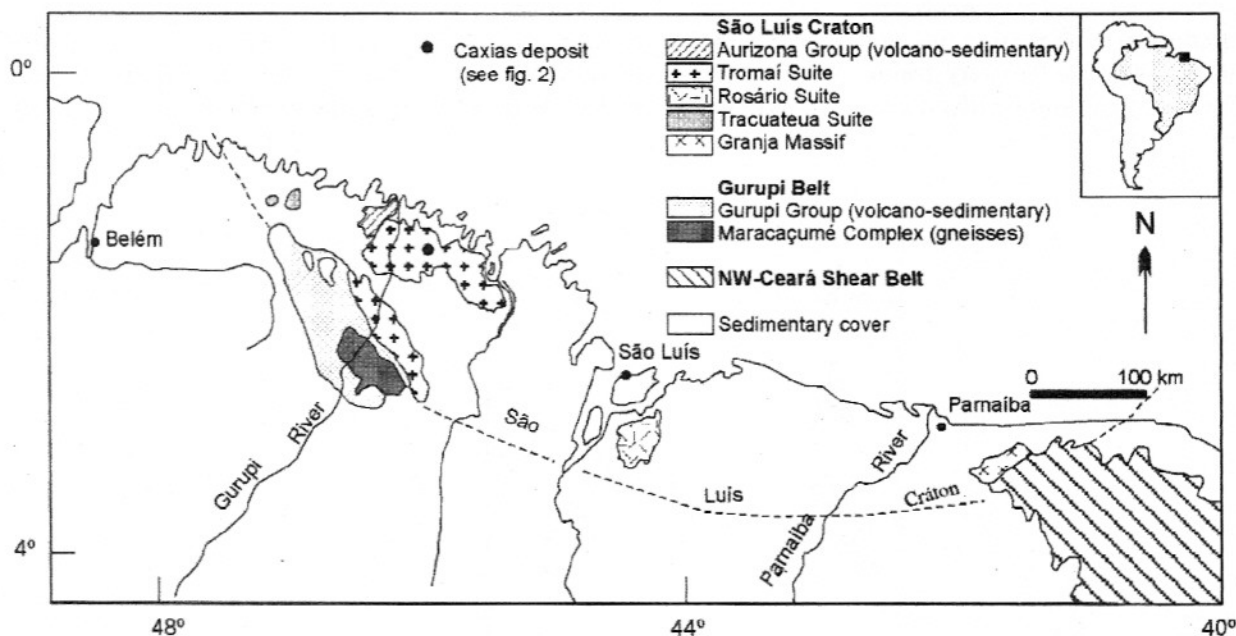
The rock samples chosen for analysis were collected from an underground work in Caxias microtonalite. One selected sample was prepared as polished thin section and described under petrographic microscope. Microprobe analyses were performed at the Universidade Federal do Rio Grande do Sul, using a Cameca SX-50 microprobe coupled with an energy-dispersion microprobe system. Analytical works were performed using 15 kV accelerating voltage and 10 seconds counting time per element. Calibration was done with natural and synthetic standards and accuracy is estimated to be 0.1%. Only the major elements were analyzed. The  $H_2O$  was calculated by stoichiometry and FeO is considered as total iron. The microprobe analyses have been recalculated on the basis of chlorite formula with 36 oxygen atoms (O, OH), 16 groups of OH and eight atoms of Si +  $Al^{IV}$ , i.e., based on 28 oxygen atoms equivalent, as recommended by Deer *et al.* (1966).  $Fe^{+3}$  was calculated according to Droop (1987).

## GEOLOGICAL SETTING

The Gurupi region in northern Brazil (Fig. 1) comprises three major geotectonic units: a cratonic area, a mobile zone and sedimentary basins (Hasui *et al.*, 1984; Pastana, 1995). The cratonic area corresponds to São Luís Craton, which is composed mainly of granitoids (Tromai, Rosário and Tracuateua suites) and metavolcano-sedimentary sequences (Aurizona Group). Geochronological data point to Paleoproterozoic ages (2000-2165 Ma) for the granitoids (Hurley *et al.*, 1967; Cordani *et al.*, 1968; Gaudette *et al.*, 1996; Gorayeb *et al.*, 1999; Klein, unpubl. data). The mobile zone corresponds to the Gurupi Belt, composed of sheared metasedimentary and metavolcanic rocks, which alternate with gneisses from a supposed ancient basement and more or less deformed to isotropic granitoids of different ages (Paleoproterozoic to Neoproterozoic). This belt has been considered as Neoproterozoic (brasiliiano), based on available Rb-Sr and K-Ar radiometric data (Almeida *et al.*, 1976; Abreu & Hasui, 1980; Abreu, 1990). Proterozoic (molassic) and Phanerozoic sedimentary basins cover both the craton and the belt areas.

## CAXIAS MICROTONALITE AND ASSOCIATED GOLD DEPOSIT

Caxias microtonalite is a small, massive, shallow intrusion, dated at  $1982 \pm 6$  Ma (Klein, 1998; Klein *et al.*, 1999). Its significance is still unclear, representing either late-stage magmatism associated with the Tromai Suite or magmatism linked to Aurizona



**Figure 1** – Simplified geological map and location map (inset) of Gurupi region, northern Brazil.

Group volcano-sedimentary sequences. It is a fine-grained equigranular rock, composed of plagioclase, quartz, biotite and minor alkali feldspar, epidote, sericite, zircon, apatite, and opaque minerals.

Gold mineralization at north-Caxias is hosted by a subvertical, NNE-striking, ductile-brittle shear zone crosscutting Caxias microtonalite (Fig. 2). In the wallrock alteration, chlorite, quartz, carbonate, white mica, pyrite and sphalerite occur after the primary mineralogy. Mineralization occurs disseminated in the host rocks and spatially associated to multidirectional quartz veining and sulfide concentrations. Fluid inclusion data, the presence of cubic and striated pyrite, the hydrothermal assemblage and the structural setting are consistent with greenschist metamorphic conditions for both Caxias rocks and hydrothermal event.

Although imprecise, the timing of gold mineralization was placed between 1737/1834 Ma and 1982 Ma (Klein, 1998; Klein *et al.*, 1999), based on Rb-Sr internal isochrons and in the crystallization age of the microtonalite, respectively.

#### Summary of fluid inclusion data

Microthermometric and laser-Raman analyses were performed in quartz veinlets crosscutting the Caxias microtonalite. Only a data summary is presented here. For a complete discussion, the reader is referred to Klein (1998) and Klein *et al.* (2000). The analyses revealed carbonic, aqueous-carbonic and aqueous populations of fluid inclusions. The aqueous inclusions were interpreted as late and unrelated to the mineralizing event, which, in turn, was related to the early carbonic

and aqueous-carbonic inclusions. These early populations show variable microthermometric properties, which were attributed to the heterogeneous trapping of two (partially) immiscible fluids and to minor post-entrapment modifications. The mineralizing fluid was defined as having the following composition: XCO<sub>2</sub>: 6-45 mol %; XN<sub>2</sub>: < 2.5 mol %; XH<sub>2</sub>O: 55-95 mol %; mean salinity of 4.5 wt % NaCl equiv.; density: 0.7-1.0 g/cm<sup>3</sup>. The final homogenization temperatures of the aqueous-carbonic inclusions have shown to be highly variable, from 205 to 378°C, and could not be used alone to define trapping conditions.

#### CHLORITE PETROGRAPHY AND COMPOSITION

Chlorites are widespread in Caxias microtonalite, occurring

as fine- to medium-grained, anhedral to subhedral elongated and slightly oriented platy grains (Fig. 3a), coexisting with quartz,

white mica, carbonate, pyrite and sphalerite, suggesting that these phases have been stable throughout the hydrothermal event. The

chlorites are colorless to olive green and show low birefringence colors. Petrographic evidence shows that they

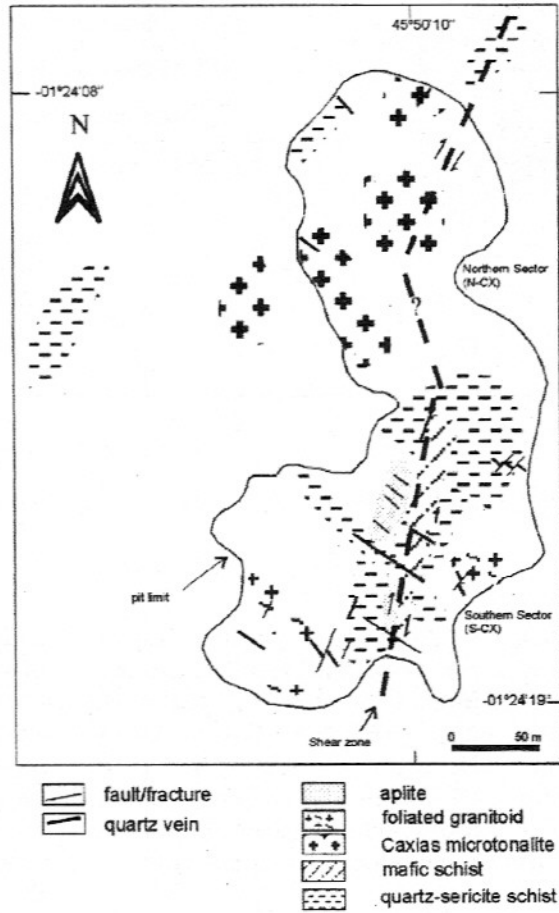


Figure 2 – Geological sketch map of Caxias gold deposit. Adapted from Klein (1998).

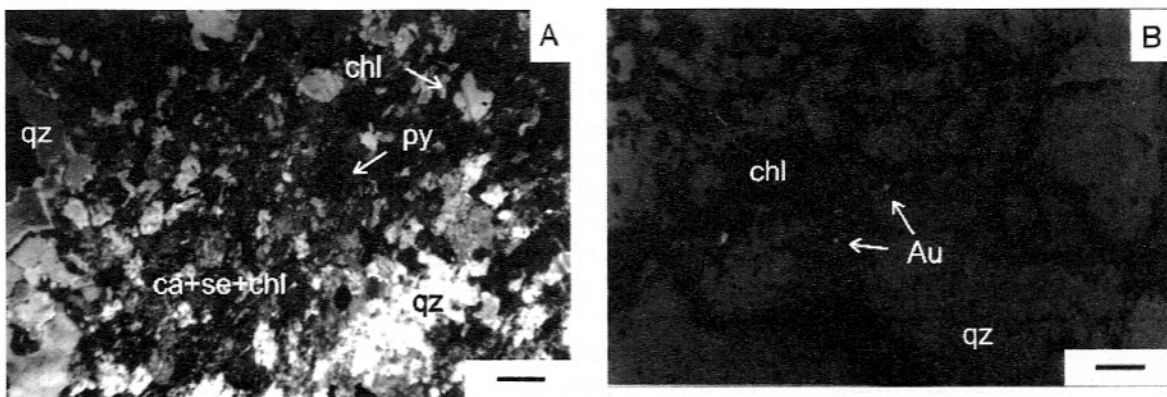


Figure 3 – Photomicrographs of Caxias microtonalite. (a) chlorite (chl) distribution along with quartz (qz), sericite (se), carbonate (ca) and pyrite (py). Scale bar: 0.4 mm. (b) gold particles (Au) in the contact of quartz (qz) and chlorite (chl) grains. Scale bar: 0.2 mm.

are the products of hydrothermal alteration of primary biotite. Free gold is present in the contact of quartz and chlorite grains (Fig. 3b) and spatially associated with sulfide concentrations.

The microprobe analytical results are given in Table 1 and show little compositional variation of the chlorites. This uniformity throughout the sample is suggestive of equilibrium between the minerals and the

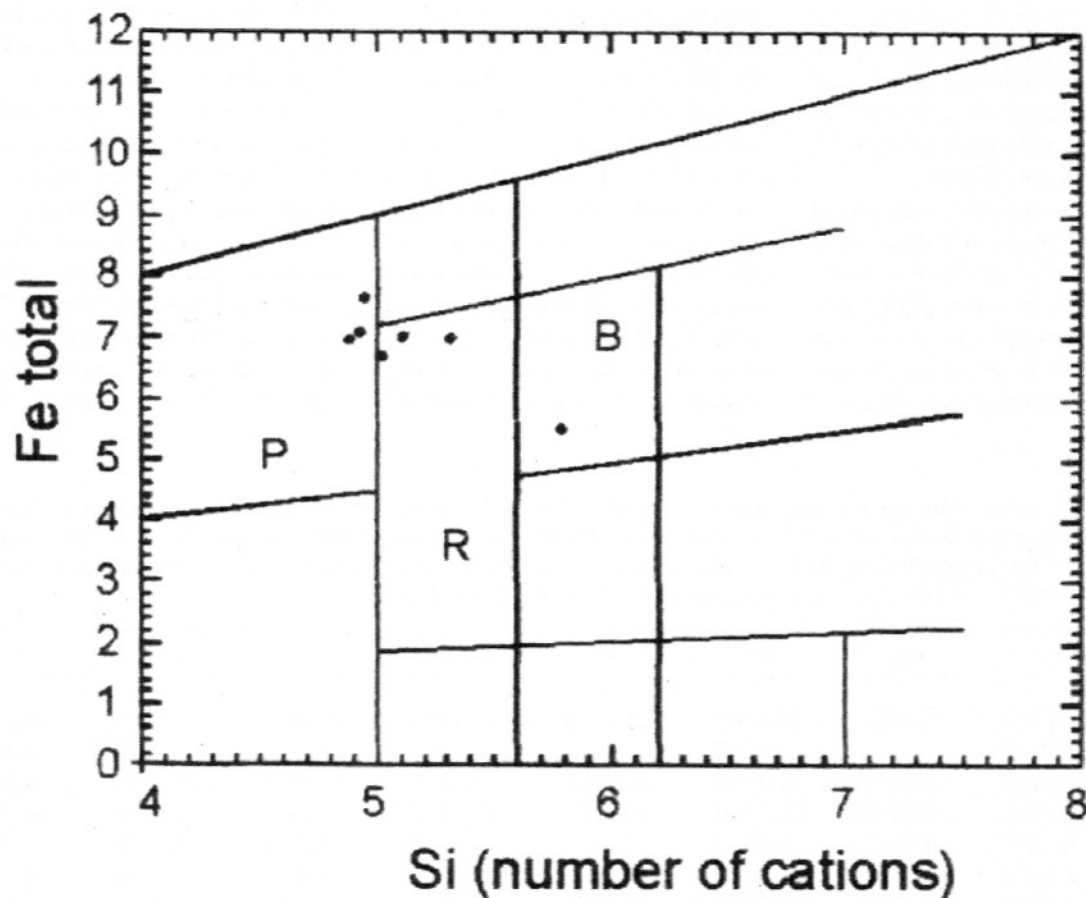
hydrothermal fluid (Neall & Phillips, 1987). The Fe/(Fe+Mg) ratio varies from 0.75 to 0.80 and Fe<sup>+3</sup>, estimated according to the procedures adopted by Droop (1987), is very low, characterizing Caxias chlorites as iron-rich and unoxidized. The Si/Al ratio shows little variability, ranging from 0.82 to 0.96, with the number of Si atoms varying between 4.92 and 5.66 and the

Al in the tetrahedral site (Al<sup>IV</sup>) varying between 2.3 and 3.0 ions per formula unit.

These relatively constant chemical characteristics allow the chlorites to be classified mostly as pseudothuringites and ripidolites (Fig. 4), according to the classification of Hey (1954). Only one chlorite differs of this behavior and plot in the field of the brunsvigite, which is a chlorite richer in Si and K. This

**Table 1** – Electron microprobe analyses (wt %) of chlorites from Caxias gold deposit. H<sub>2</sub>O calculated by stoichiometry. FeO\* as total Fe; Fe<sup>+3</sup> calculated according to Droop (1987). Temperatures (°C) calculated according to CAT: Cathelineau (1988), KM: Kranidiotis & MacLean (1987); 1: without correction of Al<sup>IV</sup>; 2: corrected for Al<sup>IV</sup> – see text for explanation), and ZF: Zang & Fyfe (1995).

	A	B	C	D	E	F	G	H
SiO <sub>2</sub>	22,0003	23,1984	22,3465	21,3102	22,1328	20,2626	20,9419	26,2120
TiO <sub>2</sub>	0,0432		0,0922		0,1954		0,0598	0,0441
Al <sub>2</sub> O <sub>3</sub>	22,7880	20,4744	22,4962	20,7382	20,8357	20,0104	21,1332	24,5926
FeO*	37,6983	36,9518	36,7408	35,2311	36,7777	36,4125	35,6540	30,6228
MnO	0,1258	0,0691	0,0474	0,1159	0,1086	0,0970	0,1158	0,0719
MgO	5,7314	5,8480	5,8879	6,6472	5,7517	5,0764	6,6592	4,5548
CaO	0,0334	0,0508	0,0115	0,0232	0,0693	0,0774	0,0231	0,0585
Na <sub>2</sub> O	0,0194							
K <sub>2</sub> O	0,0115		0,0105	0,0173	0,0345	0,0067	0,0259	1,6628
H <sub>2</sub> O	10,6732	10,4791	10,6366	10,1761	10,3581	9,7735	10,2129	11,0980
total	99,1245	97,0716	98,2697	94,2591	96,2634	91,7165	94,8529	91,9174
	cations based on 28 oxygens							
Si	4,943	5,309	5,038	5,022	5,124	4,972	4,917	5,664
Al <sup>iv</sup>	3,057	2,691	2,962	2,978	2,876	3,028	3,083	2,336
Al <sup>vi</sup>	2,973	2,827	3,011	2,777	2,805	2,754	2,761	3,922
Fe <sup>+3</sup>	0,190		0,007	0,319		0,447	0,504	
Fe <sup>+2</sup>	6,893	7,072	6,920	6,624	7,121	7,025	6,497	5,534
Mn	0,024	0,013	0,009	0,023	0,021	0,020	0,023	0,013
Mg	1,920	1,995	1,979	2,335	1,985	1,857	2,331	1,467
Ca	0,008	0,012	0,003	0,006	0,017	0,020	0,006	0,014
Na	0,008							
K	0,003		0,003	0,005	0,010	0,002	0,008	0,458
Ti	0,007		0,016		0,034		0,011	0,007
total	20,026	19,919	19,948	20,089	19,993	20,125	20,141	19,415
Oct. total	12,007	11,907	11,942	12,078	11,966	12,103	12,127	10,943
Fe/(Fe+Mg)	0,79	0,78	0,78	0,75	0,78	0,80	0,75	0,79
Si/Al	0,82	0,96	0,84	0,87	0,90	8,86	0,84	0,90
CAT	430°	371°	415°	417°	401°	426°	434°	314°
KM1	342°	303°	332°	334°	323°	339°	345°	266°
KM 2	400°	361°	390°	389°	381°	398°	400°	324°
ZF	300°	262°	291°	295°	282°	296°	307°	224°



**Figure 4** – Classification of chlorites from Caxias gold deposit, based on the diagram of Hey (1954), for chlorites with  $\text{Fe}_2\text{O}_3 < 4\%$ . P: pseudothuringite; R: ripidolite; B: brunsvigite.

could reflect either the presence of another interlayer structure (Schiffman & Fridleifsson, 1991), or an incomplete substitution of the primary biotite by chlorite.

Also, given this compositional uniformity, there is no correlation between the various chemical parameters, such as  $\text{Fe}/(\text{Fe}+\text{Mg})$  ratios when compared to  $\text{Si}/\text{Al}$ ,  $\text{Al}^{\text{IV}}$ ,  $\text{Al}^{\text{IV}}/\text{Al}$ . Good correlation was obtained between  $\text{Al}^{\text{IV}}$  and the octahedral sites vacancies, but this may represent only an artifact of the structural formula calculation. Still, the chemical composition is compatible with the composition of the trioctahedral

chlorites formed under greenschist metamorphic conditions (Xie *et al.*, 1997), confirming another previous evidence.

Comparing the chemical data of Caxias chlorites with those from other hydrothermal systems, active or fossil (Fig. 5), it is observed that they are in good agreement with those of mesothermal deposits hosted by felsic to intermediate volcanic and sedimentary sequences, such as Fazenda Brasileiro, in São Francisco Craton (Xavier, 1991) and Águas Claras, in Amazonian Craton (Silva, 1996). However, they differ from Archean lode gold de-

posits hosted by mafic-ultramafic volcanics (Neall & Phillips, 1987). They also differ from chlorites of volcanogenic sulfide deposits (Kranidiotis & MacLean, 1987), some epithermal (Walshe, 1986) and Phanerozoic, granitoid-hosted, mesothermal deposits (Trumbull *et al.*, 1996), and from active geothermal systems (Cathelineau, 1988).

## GEOTHERMOMETRY

Several workers have developed empirical geothermometers relating chlorite composi-

tion, especially the tetrahedral Al (Al<sup>IV</sup>) contents of chlorite, to its formation temperature. Equations for calculating the formation temperatures are given in Table 2.

Cathelineau & Nieva (1985) have noted a systematic increase in the Al<sup>IV</sup> contents in chlorites from active geothermal systems with increasing temperature of mineral formation and Cathelineau (1988) derived the equation 1 for temperature estimation. Besides the positive relationship between Al<sup>IV</sup> and temperature, these studies have also pointed to positive relationship between T and octahedral Fe, and to negative correlation between T and octahedral vacancies. According to Cathelineau & Nieva (1985) and Cathelineau (1988), Fe and Mg contents variation would be partially dependent on temperature and strongly dependent on the geological setting and on the solution composition.

Kranidiotis & MacLean (1987), studying volcanogenic deposits, modified Cathelineau's geothermometer adding a correction for the Al<sup>IV</sup> value, as a function of the variation of the Fe/(Fe + Mg) ratio. This ratio, in turn, would depend on the fluid to rock ratio,  $fO_2$ ,  $fS_2$ , pH, and the hydrothermal fluid composition. The expression for Al<sup>IV</sup> correction is given by equation 2 and temperature is calculated by equation 3. Kranidiotis & MacLean (1987) stressed that this geothermometer is useful in situations where chlorite grows in the presence of other aluminous minerals.

Zang & Fyfe (1995) revised these previous geothermometers and argued that for high Fe/(Fe + Mg) ratios, the calculated temperatures tend to be too high, since the calibration of the geothermometers have been done for lower ratios: <0.37

**Table 2** – Equations employed in the chlorite formation temperatures. Al<sup>IV</sup><sub>c</sub> is the corrected value for Al.

formula	Eq.
$T(^{\circ}C) = -61.92 + 321.98 Al^{IV}$	(1)
$Al^{IV}_c = Al^{IV} + 0.7[Fe/(Fe + Mg)]$	(2)
$T(^{\circ}C) = 106 Al^{IV}_c + 18$	(3)
$Al^{IV}_c = Al^{IV} - 0.88[Fe/(Fe + Mg) - 0.34]$	(4)

(Cathelineau, 1988); 0.18 – 0.64 (Kranidiotis & MacLean, 1987). Based on their own observations in deposits with high Fe/(Fe + Mg) ratio (0.78-0.81), Zang & Fyfe (1995) proposed a correction for Al<sup>IV</sup> by the equation 4, which is applied to equation 3.

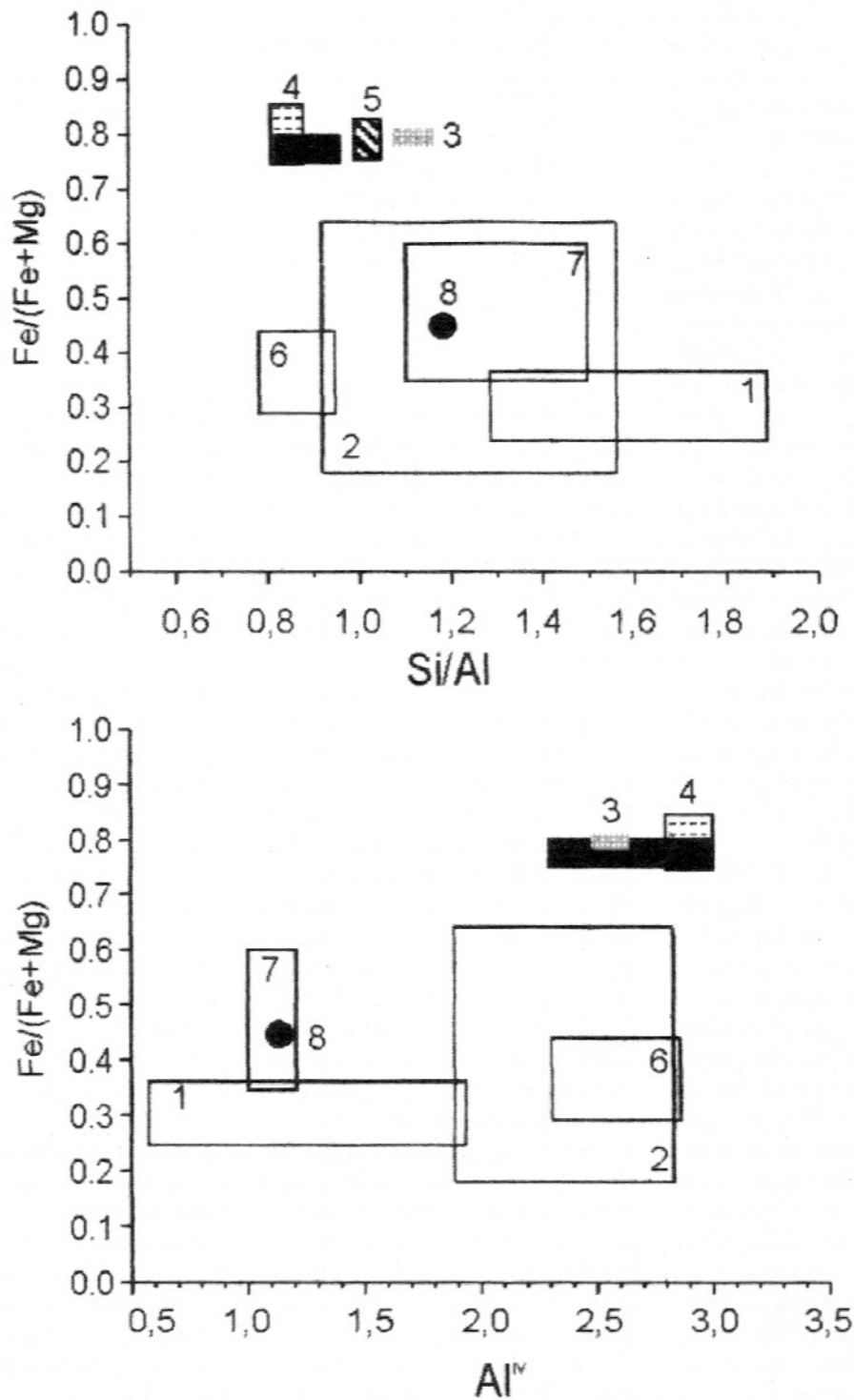
Some criticisms to these simple empirical geothermometers have been made. Jiang *et al.* (1994) argued that mixed layers and complex intergrown could exist in scales that are not detected by microprobe analysis, resulting in subtle changes in the mineral composition, especially where contamination is produced by minerals of similar formula. De Caritat *et al.* (1993) pointed to a poor composition-temperature relationship in chlorites taken from different geological settings. On the other hand, they considered these geothermometers useful when environmental conditions similar to those in which the calibration has been done, are taken into account.

Formation temperatures of the hydrothermal chlorites from Caxias microtonalite were calculated according to the three approaches presented above and the results are displayed in Table 1. A first comment is referred upon the lower temperatures calculated for chlorite H, which is K-rich and shows some octahedral vacancy. The

possibility of contamination was stated before. In fact, Schiffman & Fridleifsson (1991) documented a continuum between smectite and chlorite end-members and observed an increasing chlorite content with increasing temperature, starting with smectite below 180°C, with chlorite appearing above 270°C. Moreover, Jiang *et al.* (1994) suggested that pure chlorites show little or any octahedral vacancies and that they contain no Ca, Na and K, which are the elements responsible for consistently lower temperatures, irrespective of the employed geothermometer.

Based on this reasoning, the K-rich chlorite (analysis H) was discarded in the temperature calculations. The other analyzed chlorites are virtually devoid of Ca, Na and K, with total octahedral cations nearly the ideal figure (12, i.e., they are virtually devoid of octahedral vacancies), and they show a narrow and consistent temperature range within each geothermometer.

The second observation is that the temperatures, calculated by different geothermometers, show completely different results (Table 1). This is probably due to the different compositions presented by the chlorites used in the calibration of the geothermometer (Table 3 and Fig. 5).



**Figure 5** – Comparison between the chemical properties of chlorites from Caxias gold deposit (black filled rectangle) and from those used in the calibration of the empirical geothermometers used in this work. 1: Cathelineau (1988), from active geothermal systems; 2: Kranidiotis & MacLean (1987); 3: Zang & Fyfe (1995). The composition fields from different deposits are also displayed. 4: Fazenda Maria Preta (Xavier, 1991); 5: Águas Claras (Silva, 1996); 6: Hunt Mine (Neal & Phillips, 1987); 7: Anjiayingzi (Trumbull et al., 1996); 8: OH-vein (Walshe, 1986).



The approach of Cathelineau (1988) showed the highest calculated temperatures and Kranidiotis & MacLean (1987) and Zang & Fyfe (1995) geothermometers yielded results that did not overlap each other (Table 1 and Fig. 6), but both are compatible with the greenschist conditions. The chemical composition of the chlorites from Caxias microtonalite, especially the Fe/(Fe + Mg) ratio and the number of atoms of Al<sup>IV</sup> per formula unit, which are the parameters directly involved in temperature calculation (Eq. 2, 3 and

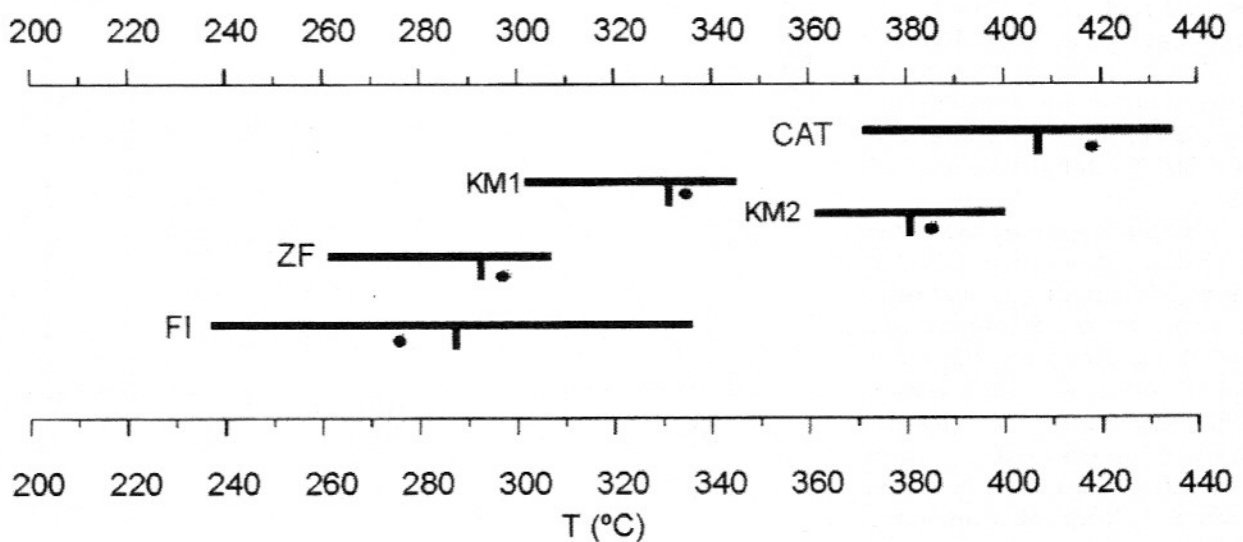
4), are remarkably similar to those used by Zang & Fyfe (1995). According to suggestion of Frimmel (1997) the geothermometer of Kranidiotis & MacLean (1987) seems to yield better results for Mg-chlorites, while the approach of Zang & Fyfe (1995) is more efficient when dealing with chlorites with Fe/(Fe + Mg) ratio greater than 0.5.

Considering the fluid inclusion data (Fig. 6), the temperature range calculated according to Zang & Fyfe (1995) overlaps the range of homogenization

temperatures recorded by the aqueous-carbonic fluid inclusions, which were defined as primary inclusions, representing the mineralizing fluid (Klein, 1998; Klein *et al.*, 2000). The results obtained according to Cathelineau (1988) and Kranidiotis & MacLean (1987), in turn, do not show any concordance with the fluid inclusion data. Furthermore, even if the temperatures are calculated without the Al<sup>IV</sup> correction (Eq. 2), the obtained values overlap only the superior extreme of the homogenization temperatures

**Table 3** – Comparison between the chemical characteristics of chlorites from Caxias deposit and from chlorites used in the calibration of the empirical geothermometers Cathelineau (1988) (CAT); Kranidiotis & MacLean (1987) (KM); Zang & Fyfe (1995) (ZF).

	CAT	KM	ZF	Caxias
Fe/(Fe+Mg)	0,24 to 0,37	0,18 to 0,64	0,78 to 0,81	0,75 to 0,80
Al <sup>IV</sup>	0,59 to 1,93	1,89 to 2,83	2,49 to 2,64	2,30 to 3,00
Si	2,80 to 3,41	5,17 to 5,80	5,36 to 5,51	4,92 to 5,66
Si/Al	1,29 to 1,89	0,92 to 1,56	1,08 to 1,16	0,82 to 0,96



**Figure 6** – Range of chlorite formation temperatures, calculated according to: Cathelineau (1988) (CAT); Kranidiotis & MacLean (1987) without correction of Al<sup>IV</sup> (KM1) and corrected for Al<sup>IV</sup> (KM2); Zang & Fyfe (1995) (ZF). (FI) is the range of fluid inclusion homogenization temperatures from Caxias gold deposit. Vertical bar is the average T and filled circle is the mode.

(Fig. 6). However, Klein (1998) interpreted these higher homogenization temperatures as representing post-entrapment modifications of the fluid inclusions (partial leakage), and not true trapping conditions.

Following the discussion above, it is considered the range of 262°C to 307°C, obtained by Zang & Fyfe's (1995) geothermometer, as the best estimate of chlorite formation temperatures at Caxias gold deposit.

### THERMODYNAMICS OF GOLD MINERALIZATION AT CAXIAS DEPOSIT

The temperature of gold deposition at Caxias is assumed to be the calculated temperature range for chlorite formation, based on the broad coincidence of this range and fluid inclusion homogenization temperatures, and in petrographic evidence that shows gold particles in the contact of quartz and chlorite grains. Combining this temperature interval with the isochores representing the lowest and highest fluid inclusion densities (Klein, 1998; Klein *et al.*, 2000), a temperature-pressure window for gold deposition is defined between 262°C and 307°C and 1.6 kb and 3.7 kb.

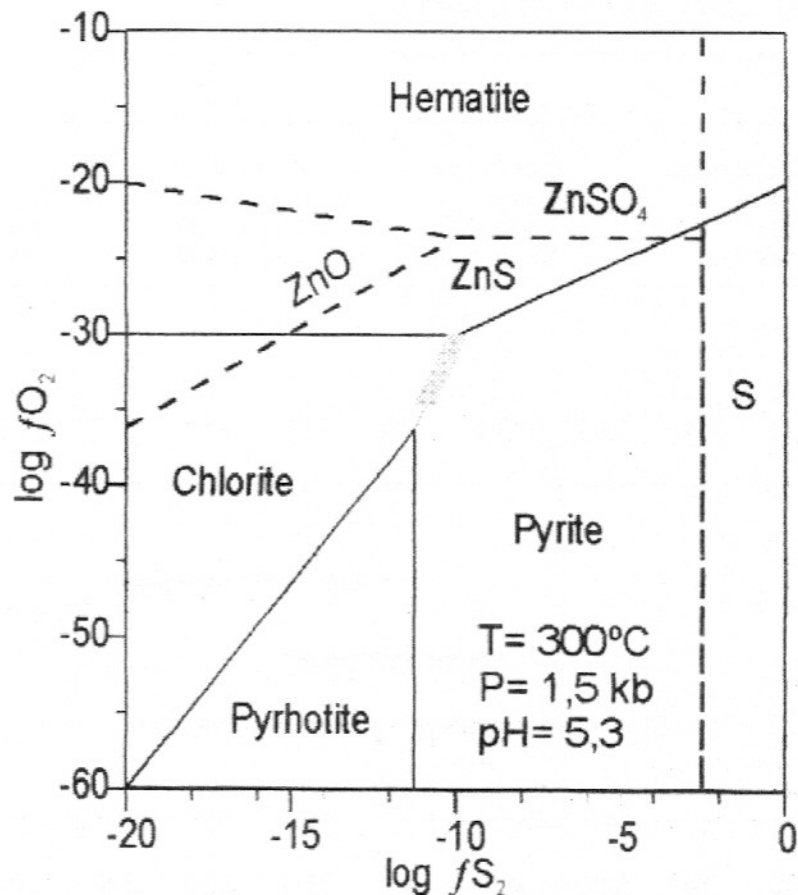
Oxygen fugacities have been calculated for the P-T-XCO<sub>2</sub> range of the hydrothermal fluid (Klein, 1998; Klein *et al.*, 2000), yielding a log  $f_{O_2}$  interval of -29.8 to -34.2, which falls between the quartz-fayalite-magnetite and hematite-magnetite buffers. This  $f_{O_2}$  interval, combined with the chlorite-pyrite mineral equilibrium and the absence of magnetite allows the estimation of log  $f_{S_2}$  between -10 and -11 (Fig. 7). Both  $f_{O_2}$  and  $f_{S_2}$

indicate relatively reduced conditions for the mineralizing fluid. Low Fe<sup>+3</sup> grades, as shown in Table 1, is also indicative of hydrothermal fluids having low oxidation state (Neall & Phillips, 1987).

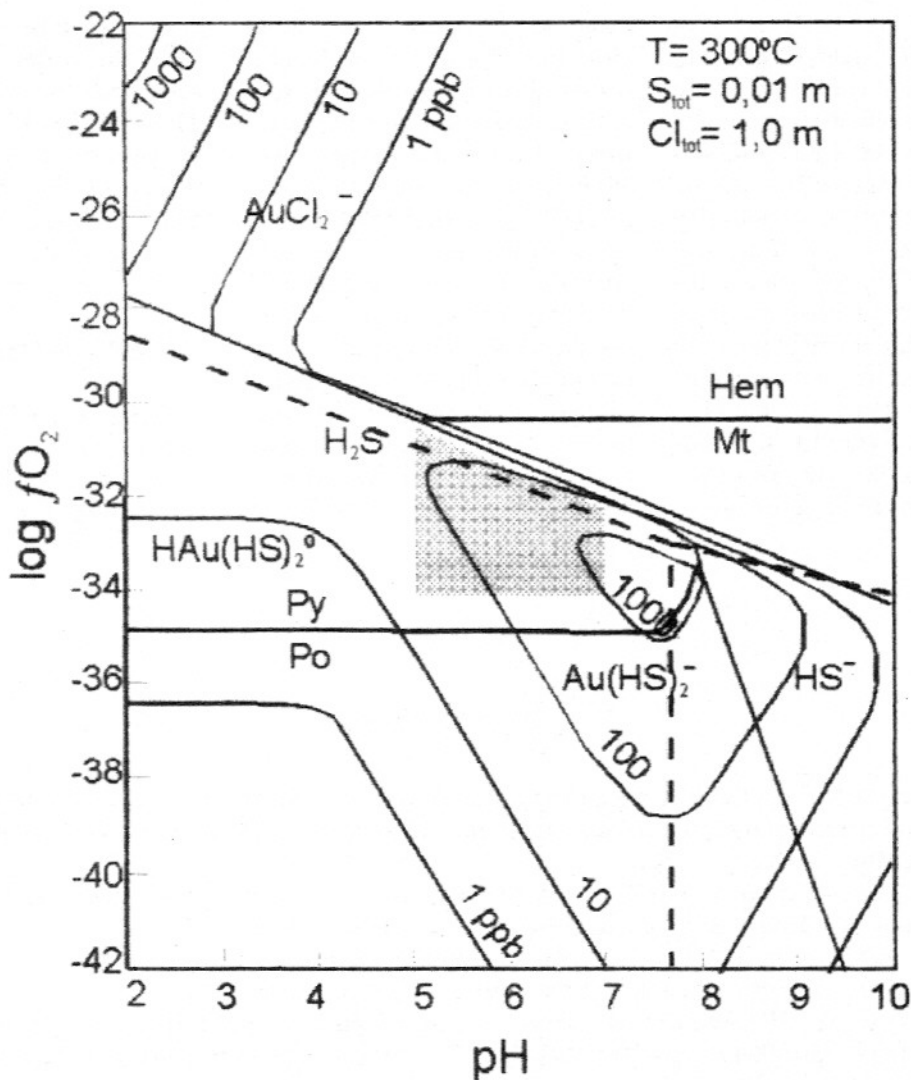
Estimates of the mineralizing fluid pH may be obtained from fluid salinity and hydrothermal paragenesis. For fluids with similar characteristics of those recorded in fluid inclusions from the Caxias deposit, Mikucki & Ridley (1993) estimated a near-neutral pH be-

tween 5.2 and 6.2. Also, a neutral to slightly alkaline pH may be inferred by the presence of carbonate (McQueen & Perkins, 1995) and white mica (Romberger, 1988) in the hydrothermal assemblage, both minerals occurring in the wallrock alteration of the Caxias microtonalite.

The calculated and estimated physicochemical conditions of the mineralizing fluid, the pyrite-chlorite coexistence, and the abundance of pyrite, suggest that gold was transported as a



**Figure 7** – Stability fields of selected mineral phases as a function of  $f_{O_2}$  and  $f_{S_2}$ , showing the redox conditions of the mineralizing fluid at Caxias, close to the pyrite-chlorite limit of coexistence. Diagram modified from Fayek & Kyser (1995 and references therein).



**Figure 8** – Gold solubility contours as a pH and  $fO_2$  function. Stability fields of auriferous complexes and of selected mineral phases are also displayed, along with the estimated conditions for Caxias mineralization (shaded area). Adapted from Hayashi & Ohmoto (1991). Hem: hematite; Mt: magnetite; Py: pyrite; Po: pyrrhotite.

reduced sulfur complex, probably  $Au(HS)_2^-$  (Hayashi & Ohmoto, 1991; Benning & Seward, 1996), as depicted from Figure 8. Gold deposition from solution have occurred in response to the breakdown of the sulfur complex by a combination of processes like separation phase, lowering of the  $H_2S$  activity by sulfidation of the host rocks, and lowering of the  $fO_2$  by diverse fluid-rock reactions.

### CONCLUDING REMARKS

Caxias is a lode-gold mineralization hosted by a shear-zone that crosscuts the Paleoproterozoic Caxias microtonalite. In the wallrock alteration, chlorite is the dominant mineral phase, occurring associated with quartz, carbonate, white mica, pyrite, sphalerite and gold.

The close association of chlorites with quartz and gold

indicates that compositional data from chlorites and fluid inclusion data on quartz, besides the knowledge of mineral paragenesis, can provide important constraints on the physico-chemical conditions of mineralization.

Three current empirical geothermometers, relating formation temperatures to Al contents on tetrahedral sites of chlorites, were employed to estimate the temperature of gold mineraliza-

tion at Caxias. The three geothermometers yielded different results, which were interpreted as caused by the differences in the composition of the chlorites used in the calibration of the geothermometers, especially tetrahedral Al and the Fe/(Fe + Mg) ratio. Among these approaches, the geothermometer of Zang & Fyfe (1995) was defined for chlorites with compositions similar to Caxias chlorites. Furthermore, the temperatures calculated by this geothermometer are in good agree-

ment with existent fluid inclusion data on quartz veinlets associated with the gold mineralization, and with the stability of the hydrothermal paragenesis. Therefore, the range of 262°C to 307°C is interpreted as the best approximation of gold deposition in Caxias deposit.

The calculated temperatures, combined with mineral paragenesis and with chlorite and fluid inclusion compositional data, allowed the estimation of relatively reduced and near neutral conditions for the mineralizing

fluid, which are compatible with the transport of gold by reduced sulfide complexes. These features are commonly encountered in mesothermal/mesozonal deposits of various ages in cratonic areas and metamorphic belts worldwide.

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