

# THE OCCURRENCE OF GOLD-RICH PYRITE IN THE ITAJUBATIBA SKARN DEPOSIT, BORBOREMA PROVINCE, NORTHEASTERN BRAZIL: A DISCOVERY BY PIXE ANALYSES

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## Introduction

Geological setting of the Itajubatiba skarn deposit

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**ABSTRACT** - The Itajubatiba deposit represents a gold skarn, in northeastern Brazil. Since its discovery in the 1940s, it was exploited during about 30 years and it has produced 5 tons of gold. Its average ore grade ranges from 0.5 to 2.0 ppm and has reached 6.3 ppm. Regional geologic units consist of a gneissic-migmatitic basement (Archean to Paleoproterozoic), a meta-sedimentary sequence (marble and schist) and Neoproterozoic intrusive igneous rocks. Later a metasomatism transformed marble, meta-tonalite (gneissic-migmatites), and meta-syenogranite into skarns. Gold mineralization is typically later, associated with sulfides, which appear either filling veins crosscutting the skarns or disseminated throughout the skarns. In order to verify this hypothesis regarding the formation of gold, a detailed search for the metal was carried out using several polished thin sections. Gold, however, was not observed. A subsequent detailed investigation of trace elements in sulfides of the Itajubatiba ore was conducted. Proton-Induced X-ray Emission (PIXE) analyses revealed that some elements occur in relatively high amounts in these sulfides, such as Mn (up to 0.9 wt.%), Au (up to 690 ppm), As (up to 1,360 ppm), Bi (0.5 wt.%), Pb (up to 1,870 ppm), Ni (up to 3,050 ppm), Co (0.6 wt.%), Se (up to 1,000 ppm), and W (up to 1,420 ppm). Pyrite shows the highest amounts of gold among the sulfides studied. Considering the quantity of gold detected in pyrite, the pyrite abundance in the study rocks, and the average densities of the main minerals occurring in skarns, their gold grade varies from 1.5 to 10.4 ppm (for gold hosted in pyrite only). The results reveal economically significant gold amounts linked to sulfides, and could provide a new perspective for the exploitation of the Itajubatiba deposit.

**Keywords:** Gold-rich pyrite, trace elements, sulfides, Itajubatiba skarn deposit, Borborema Province (Brazil).

**RESUMO** - O depósito de Itajubatiba é um exemplo representativo de skarns auríferos no Nordeste do Brasil. Este depósito foi explorado durante cerca de 30 anos e produziu 5 toneladas de ouro. O teor de ouro neste depósito varia de 0,5 a 2,0 g/t, atingindo 6,3 g/t. As unidades geológicas encontradas na região do depósito de

Itajubatiba consistem de um embasamento gnáissico-migmatítico (Arqueano a Paleoproterozoico), uma sequência meta-sedimentar (rochas metacarbonáticas e xisto) e rochas ígneas intrusivas de idade neoproterozoica. Tardiamente na evolução tectono-metamórfica, ocorreu um evento metassomático que transformou rochas metacarbonáticas, metatonalito (embasamento gnáissico-migmatítico), e metasiengranito em skarns (rochas de origem metassomática e composição cálcio-silicática). A mineralização aurífera é admitida como tendo um típico caráter tardio, ocorrendo associada a sulfetos que ocorrem preenchendo veios cortando os skarns ou disseminados na matriz dessas rochas. Com o objetivo de verificar essa hipótese, foi feita uma pesquisa detalhada por ouro visível em várias lâminas delgadas polidas, mas cristais desse metal não foram observados. Posteriormente, foi executada uma investigação detalhada das concentrações de elementos traços nos sulfetos da mineralização aurífera de Itajubatiba. As análises foram executadas por meio da técnica de Emissão de Raios-X induzida por Protons (PIXE) e revelaram que concentrações relativamente elevadas de alguns elementos químicos ocorrem nos sulfetos estudados (provavelmente na estrutura cristalina destes), como o Mn (até 0,9 %), Au (até 690 ppm), As (até 1.360 ppm), Bi (0,5 %), Pb (até 1.870 ppm), Ni (até 3.050 ppm), Co (0,6 %), Se (até 1.000 ppm) e W (até 1.420 ppm). A pirita apresentou a concentração mais elevada de ouro dentre os sulfetos analisados. Considerando-se as concentrações de ouro encontradas na pirita, a abundância deste mineral nas rochas estudadas, assim como a densidade média dos principais minerais constituintes dos skarns, revela-se que o conteúdo de ouro dessas rochas varia de 1,5 a 10,4 ppm (apenas para o ouro presente na pirita). Estes resultados denunciam teores de ouro significativamente econômicos nos sulfetos, e lançam uma nova perspectiva para a exploração do depósito de Itajubatiba.

**Palavras-Chave:** pirita aurífera, elementos traço, sulfetos, depósito de skarn de Itajubatiba, Província Borborema (Brasil).

## INTRODUCTION

Gold commonly exhibits a characteristic known as “invisible” in its mineral deposits. In these cases, gold concentrations are apparent in the geochemical analyses of bulk samples, yet gold crystals are not seen by means of classic optical microscopy. The metal usually occurs as submicrometer-size inclusions (less than 1  $\mu\text{m}$  in size) of native gold in other ore minerals (e.g. sulfides), or as a trace element (structurally bound Au) in the sulfide composition (e.g. arsenopyrite) - (Boyle, 1979; Cook & Chryssoulis, 1990; Genkin et al., 1998; Pals et al., 2003). In such cases, chemical microanalyses of sulfides can reveal the real way in which the gold is occurring, in addition

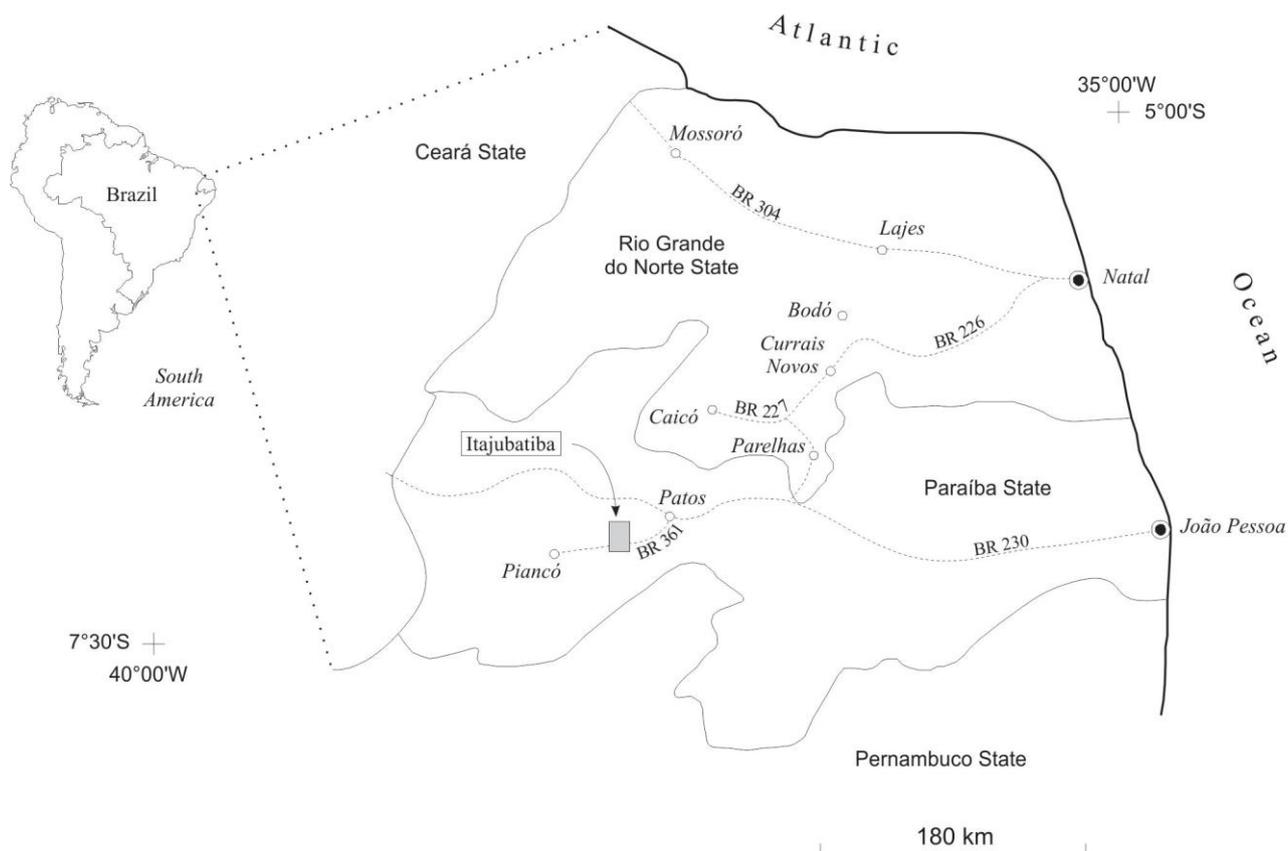
to providing a useful guide for the extraction of the metal.

In this study, PIXE analyses were carried out to determine contents of trace elements within the sulfides from the Itajubatiba skarn deposit. The main objective of these analyses was to establish the distribution of the mineralizing elements (e.g. Au, Ag, and Bi) in the ore minerals. This allows us to investigate the possible source of the ore elements present in the mineralization by means of the geochemical association, as well as to find the mode of occurrence form of the gold, since this metal was not observed in an exhaustive observation of polished thin sections.

## GEOLOGICAL SETTING OF THE ITAJUBATIBA SKARN DEPOSIT

The Itajubatiba deposit is situated 35 km southwest of the town of Patos in the Paraíba state, northeastern Brazil (Figure 1). It was discovered in the 1940s and was mined over a thirty-year period, with a total production of approximately 5 tonnes of gold. The ore grade ranged from 0.5 to 2.0 ppm and the highest grade reached 6.3 ppm (Rebouças, 1985). This

deposit is located in the northeastern portion of the Borborema Province (BP), within the Patos Shear Zone (PSZ). At the BP, NE-SW and E-W strike-slip shear zones dominate the tectonic features, having been caused by a transpressional tectonic episode that was active during the Brasiliano/Pan-African orogeny, around 600 Ma (Archanjo, 1993).

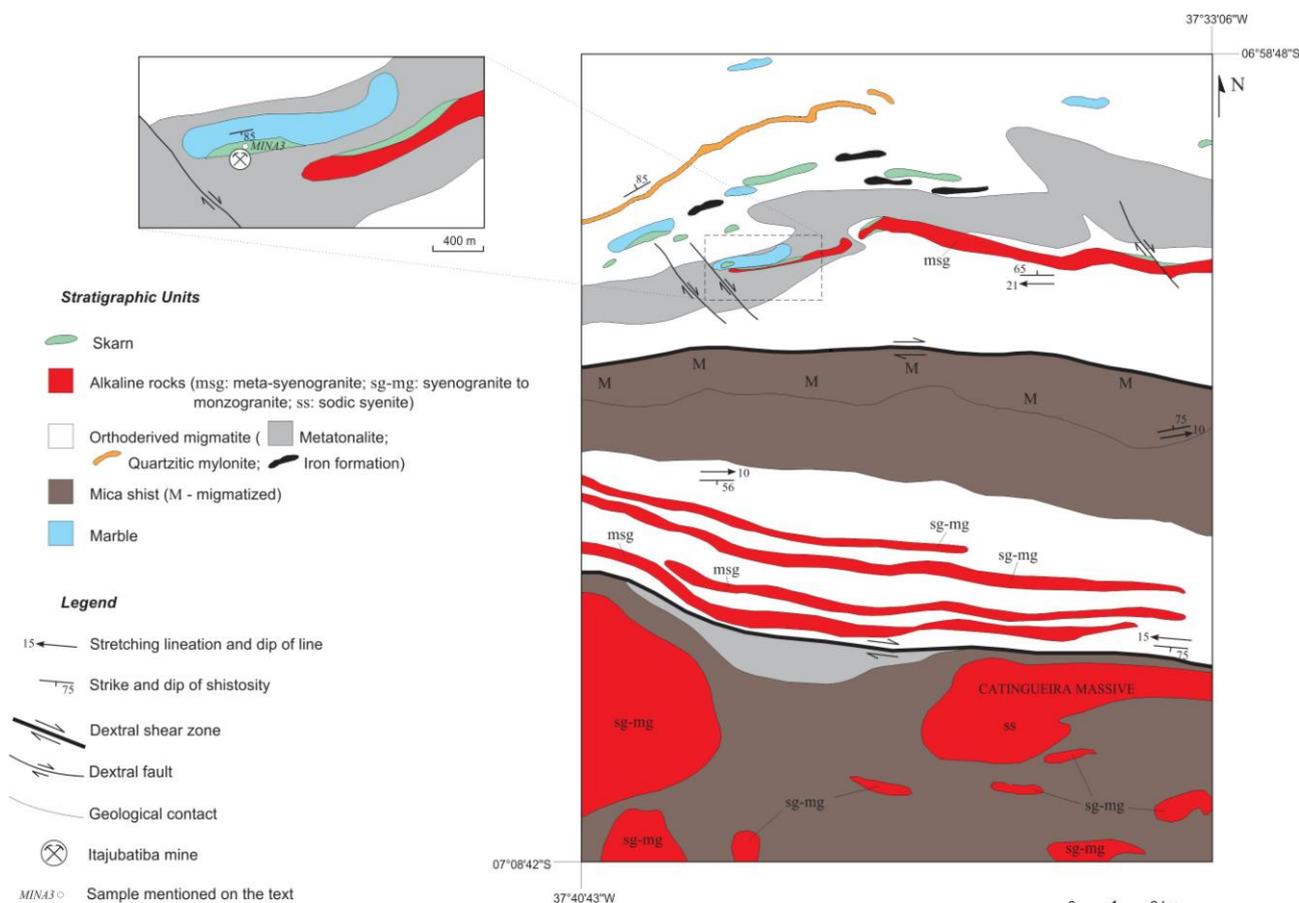


**Figure 1.** Localization of the study area in the Itajubatiba skarn deposit, in Northeastern Brazil.

Geological units occurring in the Itajubatiba area can be summarized as follow: migmatitic gneisses, marble, schist, alkaline igneous rocks, skarns, and pegmatites. The migmatitic gneisses are correlated with the Paleoproterozoic-Archean rocks, and can be subdivided into four groups, according to their melanosome mineralogy and texture, as follow: (i) monzogranite to granodiorite and augen gneiss, (ii) meta-tonalite, (iii) hornblende-biotite gneiss, and (iv) porphyritic monzogranite. The meta-tonalite contains two lithological variations: amphibole-rich meta-tonalite and quartz-garnetite (Figure 2).

Marble and schist correspond to the supracrustal rocks of the Seridó Group (Jucurutu and Seridó Formations, respectively). Their deposition probably occurred *ca.* 610–

650 Ma (Van Schmus et al., 2003), or during the interval of 573–640 Ma (Nascimento et al., 2004). Marble reefs or lenses occur as tectonic bodies 2–250 m thick, shear bounded, within meta-tonalites. They are of two types, phlogopite- and olivine-bearing marbles. The former presents calcite, phlogopite, tremolite, talc, graphite, and apatite. The olivine-bearing marble preferentially occurs around the skarns (outer zone), and is composed of calcite, olivine, talc, hercynite, apatite, and allanite. Serpentine and clinohumite also occur, and were formed by olivine replacement. The schist is fine-grained and is constituted by plagioclase, quartz, biotite, garnet, cordierite, sillimanite, muscovite, and minor graphite, tourmaline, apatite, and zircon.



**Figure 2.** Geologic map of Itajubatiba skarn deposit (simplified from Souza Neto, 1999).

In some places, this schist is intensely migmatized, forming mainly a coarse-grained rock that contain alkali feldspar, biotite, plagioclase, quartz, garnet, graphite, zircon, apatite, and tourmaline, as well as sillimanite and muscovite as late phases.

The alkaline igneous rocks are correlated to the Neoproterozoic magmatism, which is found in the Seridó Metapelitic Belt (SMB), with ages varying from 555 to 610 Ma (Legrand et al., 1991; Jardim de Sá et al., 1999). At Itajubatiba, they have been grouped into the following categories: (i) meta-syenogranite, (ii) syenogranite to monzogranite, and (iii) sodic

syenite. Numerous pegmatites crosscut all other lithologies, including the skarns. In the SMB, the pegmatites have ages of 510-450 Ma (Ebert, 1970). Recent data show ages of  $520 \pm 10$  Ma (U-Th-Pb EMPA dating of uraninite, xenotime, and monazite; Beurlen et al., 2009);  $509.5 \pm 2.9$  Ma and  $514.9 \pm 1.1$  Ma (U-Pb dating of columbite; Baumgartner et al., 2006);  $523 \pm 2.5$  Ma ( $^{40}\text{Ar}$ - $^{39}\text{Ar}$  dating of biotites; Araújo et al., 2005), and  $525.7 \pm 1.4$  Ma and  $532.9 \pm 1.9$  Ma ( $^{40}\text{Ar}$ - $^{39}\text{Ar}$  dating of micas; Araújo et al., 2003) for these pegmatites.

## SKARNS AND GOLD MINERALIZATION

At Itajubatiba, the skarns were formed by metasomatism that occurred after the last tectono-metamorphic phase (Brasiliano Orogeny), mainly indicated by the irregular and interdigitating contacts between the skarns and their country rocks. The skarns occur along the main structural trend, and constitute massive

bodies without foliation. In some places, the skarns can show a banding, which is attributed to the metasomatic zoning.

By considering their relationship with the granitoid rocks a tentative age from 555 to 450 Ma can be attributed for the skarns. This interval corresponds to the lower age of the

igneous rocks (maximum value of that), which are considered to be the source of parental fluid evolved in the skarn formation, and the age of late pegmatites (minimum value), which crosscut the skarns (see the description of the skarns developed after meta-syenogranite, below).

Three types of skarns have been recognized at Itajubatiba: skarns developed after marble, those developed after meta-tonalite, and others developed after meta-syenogranite (Souza Neto, 1999; Souza Neto et al., 2008). The metasomatic columns (from the original substrate towards the inner skarn) for each skarn type can be summarized as follows:

- Skarns developed after marble: phlogopite-bearing marble / olivine ( $\text{Fo}_{86-94}$ )-bearing marble (skarn outer zone) / amphibole (tremolite and actinolite) zone (skarn) / pyroxene ( $\text{Di}_{24-93} \text{Jo}_{0-2}$ ) zone (skarn);

- Skarns developed after meta-tonalite: meta-tonalite / amphibolitized meta-tonalite (skarn outer zone) / amphibole (ferrotschermakite, ferrohornblende, and magnesiohornblende) zone (skarn) / pyroxene ( $\text{Di}_{24-93} \text{Jo}_{0-2}$ ) - plagioclase zone (skarn) / garnet ( $\text{Gross}_{1-25} \text{And}_{3-13} \text{Alm}_{61-72} \text{Py}_{\text{up to } 10}$ ) zone (skarn), and

- Skarns developed after meta-syenogranite: meta-syenogranite / calc-silicate-bearing meta-syenogranite (skarn outer zone) / amphibole (magnesiohornblende to actinolite) zone (skarn) / pyroxene ( $\text{Di}_{24-93} \text{Jo}_{0-2}$ ) - plagioclase ( $\text{An}_{20-30} \text{Or}_1 \text{Ab}_{68-78}$ ) zone (skarn) / garnet ( $\text{Gross}_{34-46} \text{And}_{45-57} \text{Alm}_{3-5}$ ) zone (skarn).

Skarns developed after marble are medium to coarse-grained and occur as interlayered pyroxene-rich lenses (0.1-10 m thick) within phlogopite-bearing marble. Apart from minerals of the main skarn zones, the mineralogical composition of this type of skarn is represented by variable amounts of epidote, titanite, apatite, allanite, calcite, magnetite, pyrrhotite, pyrite, chalcopyrite, and minor arsenopyrite. Sulfides occur disseminated or in fractures crosscutting the skarns. Quartz veins and calcite-epidote-filled fractures often crosscut the skarns.

Skarns developed after meta-tonalite, occur in direct contact with it, or at the meta-tonalite-marble contact. This skarn occurs as massive and banded bodies 1-5 m thick. A typical ore-

bearing sample, based on descriptions of Rebouças (1985), contains amphibole-pyroxene- and garnet-rich bands (about 6 mm thick) with regular alternation. This banding probably reflects the fact that the contacts between the skarn zones are not sharp, where the zones get to invade one another. In this ore sample, interstitial hematite occurs, while pyrrhotite-chalcopyrite-pyrite appears disseminated within the amphibole-rich bands. Quartz-calcite and calcite-biotite as discordant veins, and associated sulfides also occur. The main quartz-calcite-sulfide veins show a typical alteration halo (up to 3 cm wide) of light green colour, composed by calcite (interstitial texture) and sericitized plagioclase.

Skarns formed on meta-syenogranite bodies are 20-40 m wide and up to 400 m long, mainly along the shear-controlled margins of their parental intrusions. They are medium to coarse-grained and show a banding defined either by alternating garnet-plagioclase- and pyroxene-epidote-rich bands, or garnet-pyroxene- and amphibole-rich bands. Scapolite occasionally appears in this skarn instead of plagioclase. This skarn type often contains titanite (up to 1 cm in length), and  $\pm$  apatite, allanite, quartz, calcite, and opaque minerals. These last three minerals exhibit interstitial textures, indicating their late character. Pegmatite bodies (up to 15 cm wide) crosscut this skarn, enclosing small fragments of it. Many quartz veins (0.5-20 cm thick) present stockwork structure. Some veins on the contrary are typically quartz-filled fractures distributed along the N-S direction, which controls the shape of the blocks of skarn. Many quartz-calcite, amphibole-calcite and amphibole-quartz-sulfide micro-veins also occur. These last veins show a halo where the plagioclase of the surrounding rock is intensely altered (hydrothermal process).

Gold at Itajubatiba occurs either disseminated within the calc-silicate gangue of the skarns, or in quartz veins (Lins & Scheid, 1981; Rebouças, 1985). In the present research, gold was not seen in any studied samples, although many samples (about 30 polished thin sections) have been analysed for this purpose. Thus, the gold is considered possibly to be associated with sulfides, which

are observed either disseminated within, or filling tension-gash fractures (associated with quartz-calcite) crosscutting the skarns.

In the SMB, gold mineralization hosted in quartz veins (mainly within schists of the Seridó Formation) is considered Cambro-Ordovician and to have formed during two episodes: 510-520 Ma and 500-506 Ma (Araújo et al., 2003). These ages could also be considered valid for the gold mineralization in the skarns, since both mineralizations (hosted in schists and in skarns) seem to be coevally formed, as suggested by their coincident structural style (controlled veins).

In the SMB, all the skarns occur related to the marble and paragneiss of the Jucurutu Formation. They occur preferentially at the marble-paragneiss contact, or within the marble

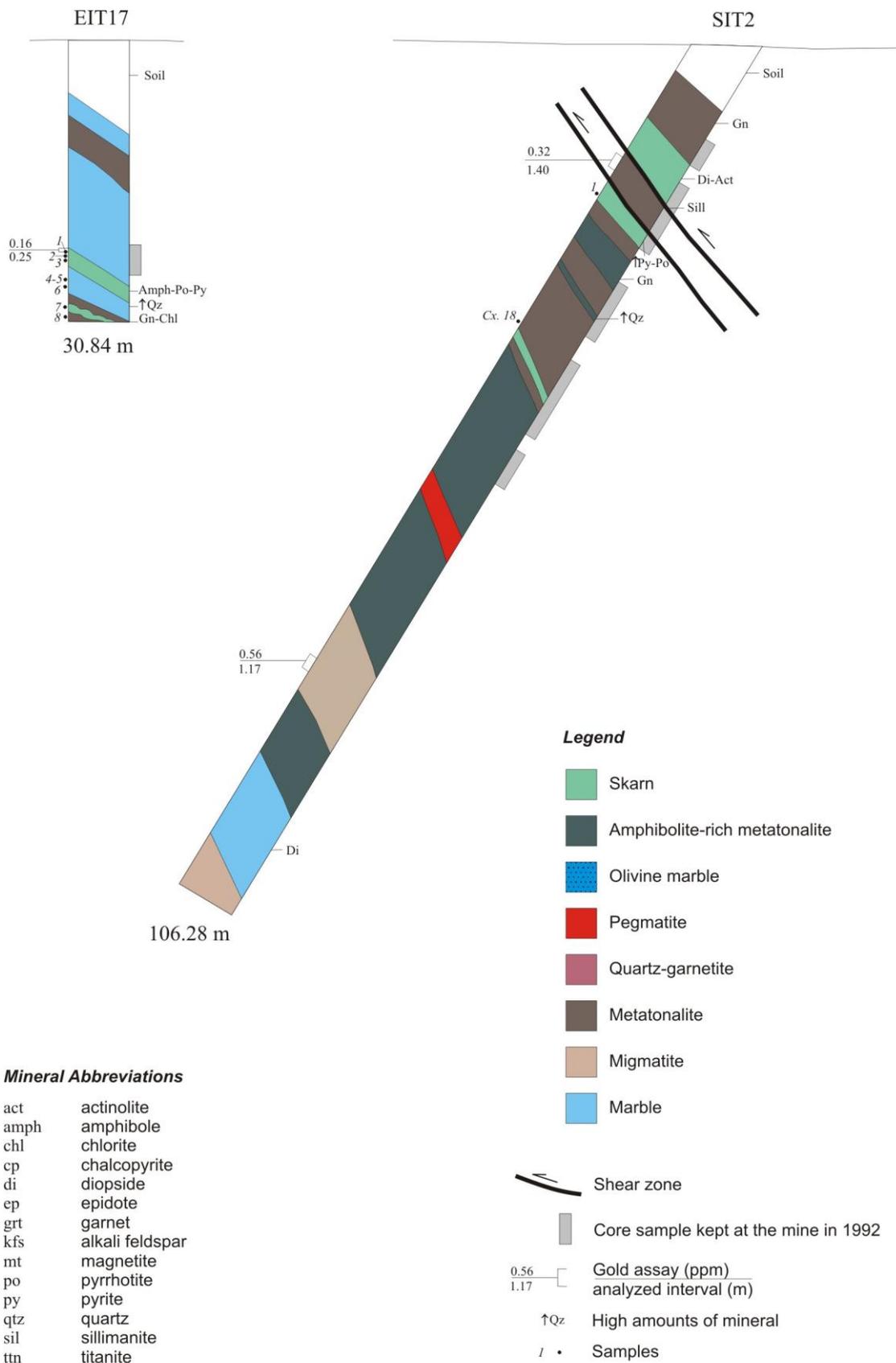
(Souza Neto et al., 2008). Most skarns are W-Mo mineralized (e.g. Brejuí and Bodó, located at Currais Novos and Bodó towns, respectively, in Rio Grande do Norte state). Only one known skarn deposit (Bonfim, located in the Lajes county, in Rio Grande do Norte state) contain both, W-Mo and gold mineralizations. In later case, gold mineralization is clearly late with respect to the W-Mo ones, since it occurs filling fractures (tension gash) that crosscut the W-Mo-bearing minerals (Souza Neto et al., 2008). In this context, the Itajubatiba skarns is the only case known that contains exclusively gold, with some trace contents of W reported (Lins & Scheid, 1981; Rebouças, 1985; Souza Neto et al., 2008).

## PIXE ANALYSES OF SULFIDES

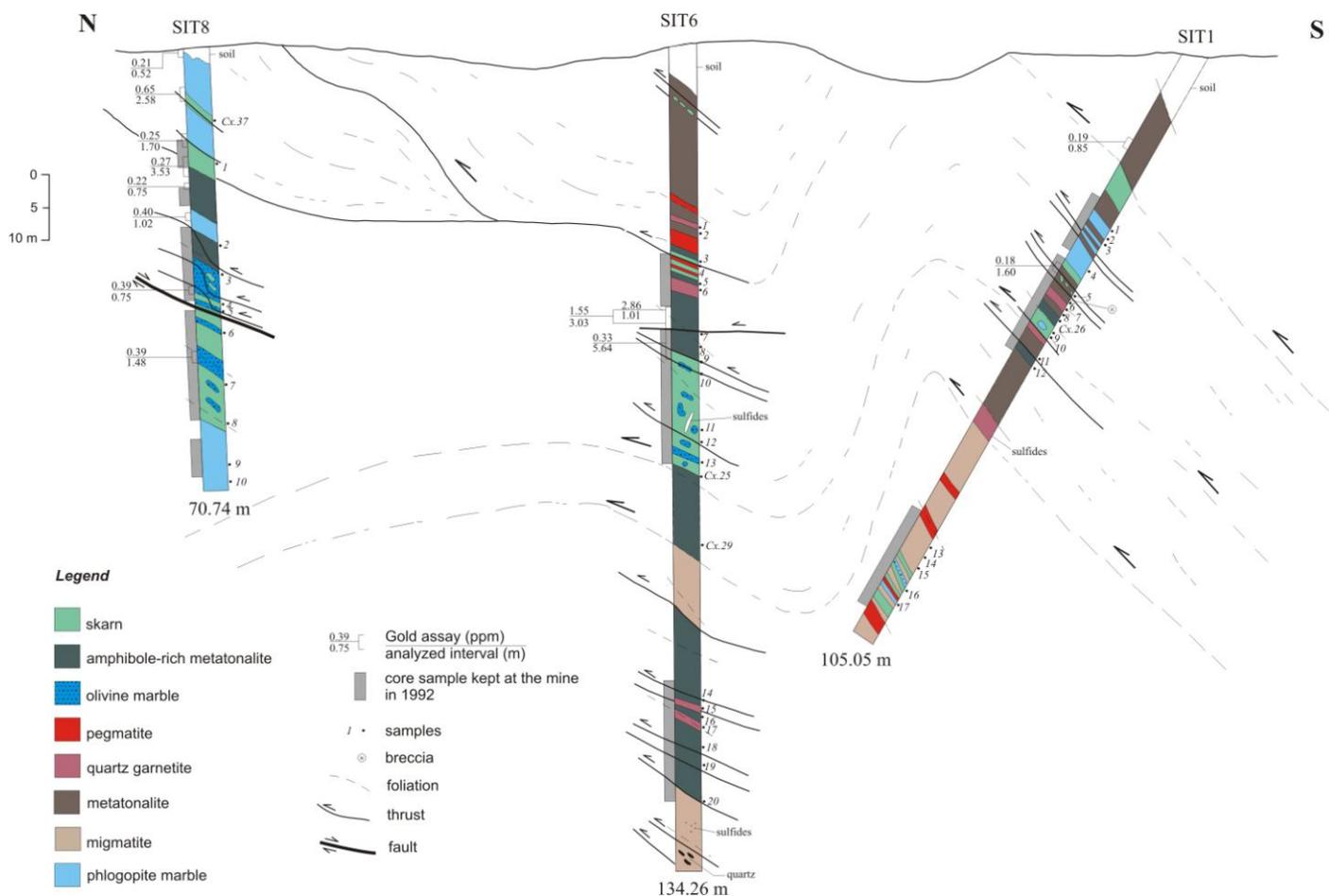
### Samples and analytical procedures

Seven representative samples of the Itajubatiba skarn deposit were used. Four samples of skarns (MINA3 collected at the mine site, and SIT2/1, EIT17/1, and SIT8/Cx37 from the drill cores SIT2, EIT17, and SIT8, respectively; Figures 2, 3, and 4). Two samples of quartz-garnetite (SIT1/8 and SIT6/15 from the drill cores SIT1 and SIT6, respectively; Figure 4) and the last sample from quartz-calcite vein crosscutting amphibole-rich meta-tonalite (SIT1/Cx26 from the drill core SIT1; Figure 4). The samples for PIXE analyses were prepared in polished thin sections, 100  $\mu\text{m}$  wide. Among the microanalytical techniques, the Proton-Induced X-Ray Emission (PIXE) is a non-destructive

technique that allows measuring trace elements in minerals. The principle of the PIXE method consists of bombarding a target with a beam of protons ( $\text{H}^+$ ) or heavy ions (e.g.  $^2\text{H}^+$ ) produced by a particle accelerator (synchrotron). The coulomb interaction promoted by this beam produces electron vacancies in the deep layers of the atoms. The re-arrangement of the electrons in these layers leads to an x-ray emission that has a characteristic wavelength according to the atom from which this x-ray was emitted. In the PIXE method, the highly intense proton beam from the synchrotron, however, allows deep atoms can excited by the protons remaining after the attenuation by the matrix (Fraser, 1995; Volfinger et al., 1997).



**Figure 3.** Representative drill cores (SIT2 and EIT17) from Itajubatiba skarn deposit with localization of the samples mentioned on the text (simplified from Souza Neto, 1999).



**Figure 4.** Representative geological section of the Itajubatiba gold deposit, obtained by description of drill core (SIT8, SIT1, and SIT6) samples (simplified from Souza Neto, 1999).

PIXE analyses were carried out using a proton miniprobe at the CERI laboratory of the *Centre National de la Recherche Scientifique (CNRS)*, in Orléans, France. Analytical conditions were: 2.5 MeV proton beam, with a spot of 1,500  $\mu\text{m}^2$ , and a current intensity of 0.7-0.8 nA. Calibration was undertaken with glass (Si), and pure metals/alloys (Ti, Fe, Zn, Zr, Mo, Ag, Cd, and Pt-Rh). The x-ray spectrum analysis was quantitatively performed by fitting the results to the database of a modeling program (Maxwell et al., 1988). Some samples in which Fe, As and Cu constitute major elements, were semi-quantitatively measured, because PIXE analysis is not calibrated for high concentrations.

### Results and discussion

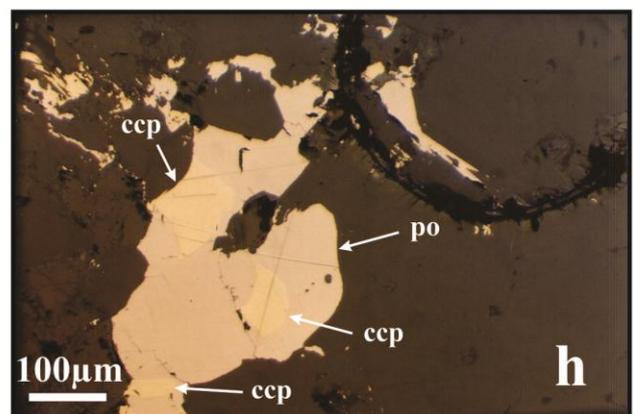
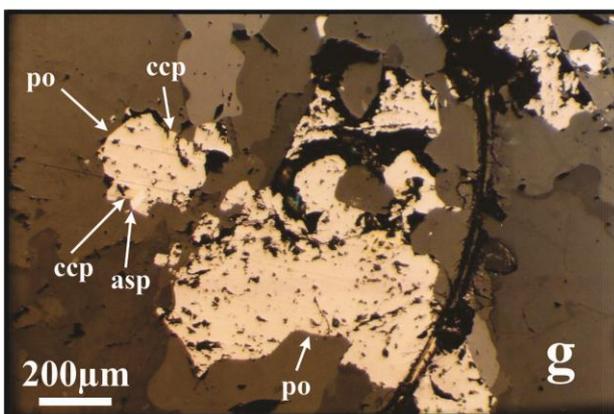
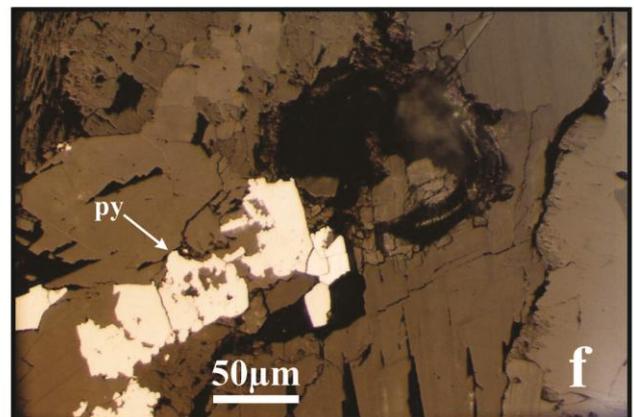
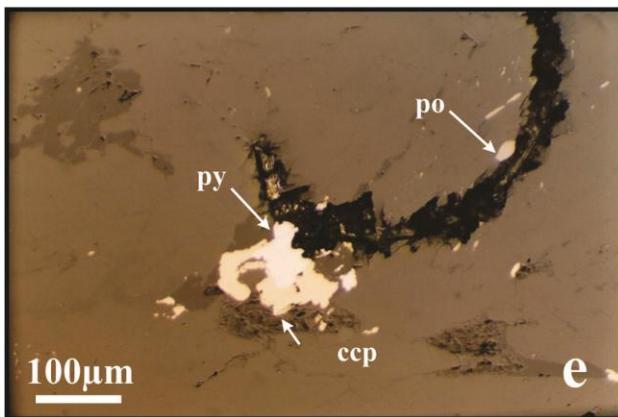
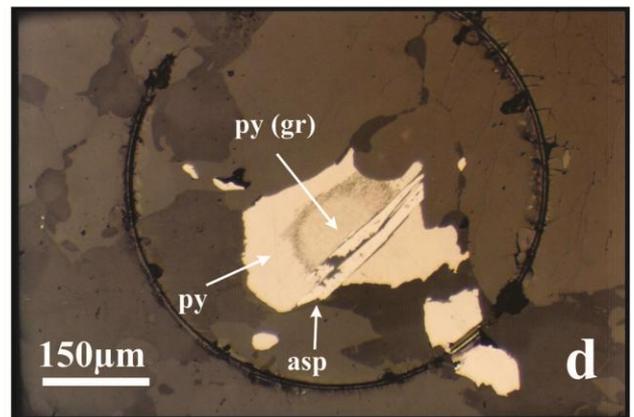
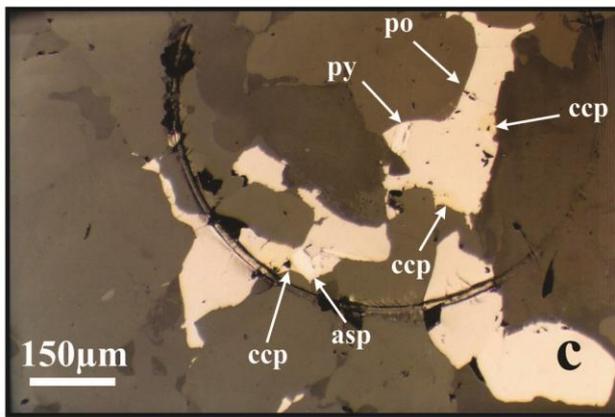
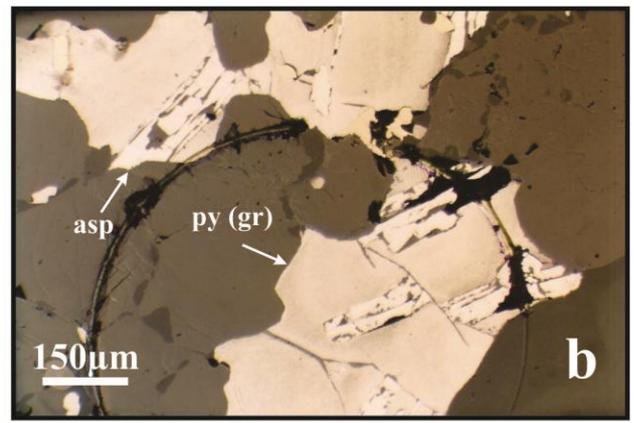
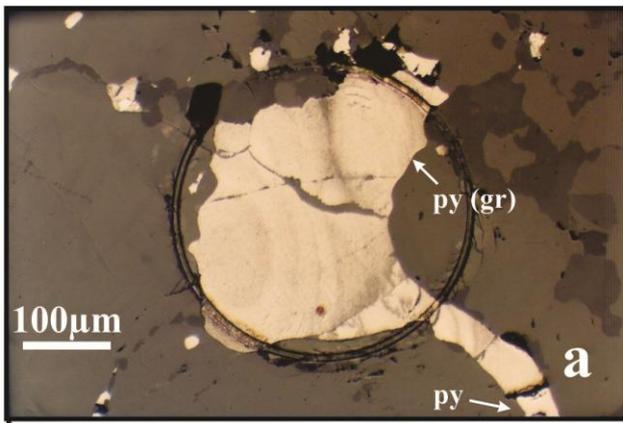
Table 1 gives the PIXE results obtained from sulfides of the Itajubatiba skarn deposit. The main elements detected were: Mn (0.5-0.9 wt.%), Au (200-690 ppm), As (242-1,360 ppm), Bi (0.5 wt.%), Cu (580 ppm-17.3 wt.%), Pb (180-1,870 ppm), Ni (510-3,050 ppm), Co

(0.6 wt.%), In (95-200 ppm), Se (96-1,000 ppm), and W (up to 1,420 ppm). Among these elements, Au, As, Pb, Ni, and Se show the higher frequency of occurrence. From a total of twelve analyses carried out, these elements appeared in 7, 7, 8, 9, and 11 cases, respectively. The highest gold amount (690 ppm) was found in the granular textured zone (alteration ?) of a pyrite crystal (Figure 5). It must be noted that examples worldwide of unusually high “invisible” gold record up to 1,400 ppm Au in pyrite (Fairview gold deposit, South Africa; Fleet et al., 1993), and up to 4,000 ppm Au in Fe sulfides (Carlin-type gold deposits; Hofstra and Cline, 2000). Anomalously high concentrations of “invisible” gold reported reach up to 3 wt.% Au in pyrite (Carlin-type Screamer deposit; Palenik et al., 2002).

**Table 1.** PIXE analyses of sulfides from representative samples of skarns and country rock of the Itajubatiba skarn deposit. Value format: 0.0 (wt.%) and 0,000 (ppm). The symbol "<" present in some cases means that the respective element was detected, but could not be quantified because its quantity was below the detection limit of the analyses. Blank refers to elements not detected.

Sample	SIT8/Cx37	SIT2/1	EIT17/1	MINA3	SIT2/1	MINA3	SIT2/1	SIT2/1	SIT2/1	SIT1/8	SIT6/15	SIT1/Cx26
Depth (m)	(10)	(20.6)	(23.5)	outcrop	(20.6)	outcrop	(20.6)	(20.6)	(20.6)	(43)	(106.5)	(44.7)
Rock type	SkM	SkMet	SkMet	SkMet	SkMet	SkMet	SkMet	SkMet	SkMet	QzG	QzG	Vein
Mineral	asp	ccp	ccp	po	po	py	py	py	py (gr)	py	py	py
Fe	39.4	41.2	31.5	63.5	60.4	47.3	49.2	54.7	48.7	41.6	25.8	46.2
Mn				0.9		0.5						
Au		< 190	< 140		< 250		< 80	200	690			620
Ag		< 60	< 40									
As	9.6	1,360		242	1,000		< 110	730	< 125			
Bi										0.5		
Cu		27.1	55.3		< 120	17.3		580		16.6		
Pb		< 140	< 120		< 490		180	< 220	< 80		220	1,870
Zn			< 850									
Ni	603	< 210			2,520	530	1,070	3,050	1,170		510	820
Co	0.6											
In		< 55			200		< 80		< 60		95	
Se		210	215	96	120	846	280	300	270	1,000	750	540
W					< 175		< 400	< 280	< 410			1,420

**Abbreviations:** QzG quartz-garnetite; SkM skarns developed on marble; SkMet skarns developed on metatonalite; Vein quartz-calcite vein crosscutting amphibole-rich meta-tonalite. **Mineral abbreviations** (according to Kretz (1983) and Spear (1993)): apy arsenopyrite, ccp chalcopyrite, po pyrrhotite, py pyrite, py (gr) granular pyrite.

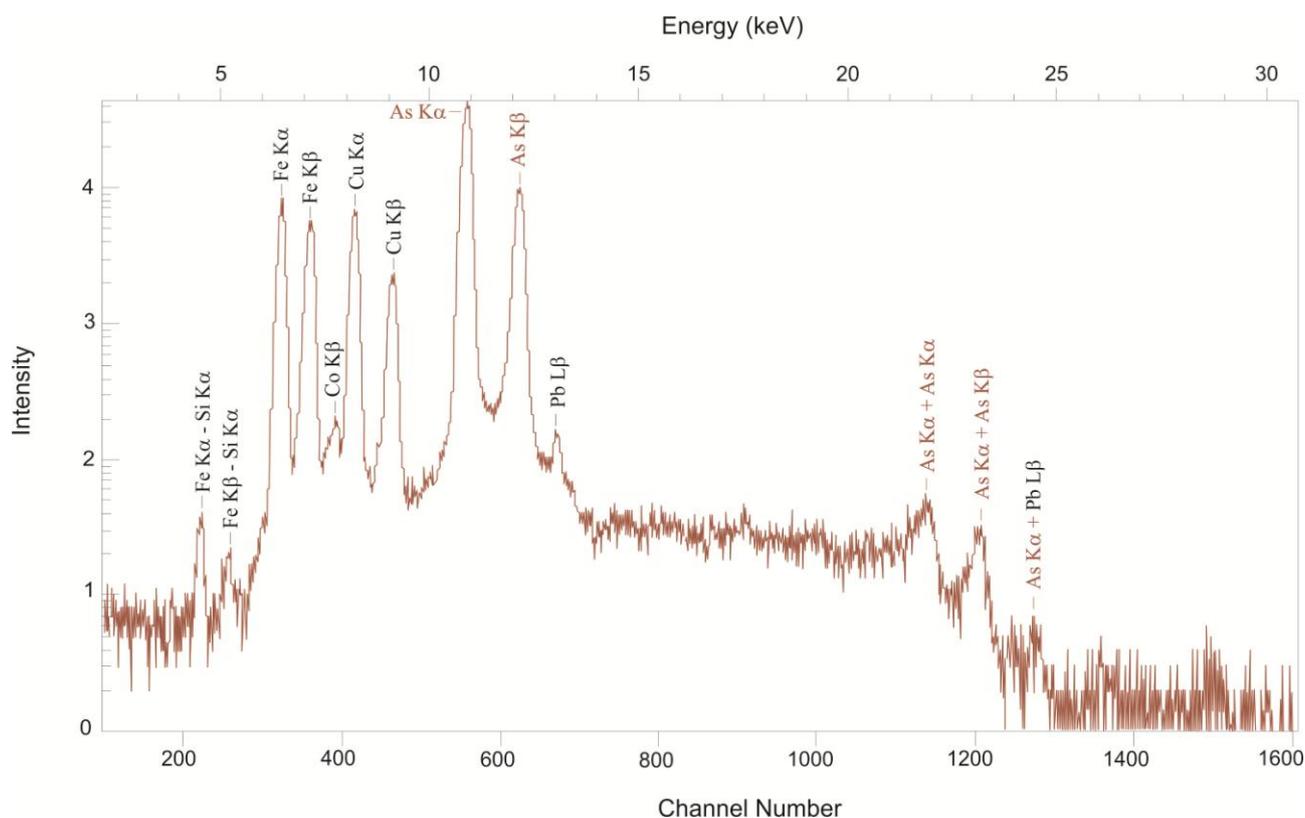


**Figure 5.** Photomicrographs showing sulfides from the Itajubatiba skarn deposit, Borborema Province, northeastern Brazil. (a) Granular textured zone (py (gr); alteration ?) of a pyrite crystal

(py) disseminated within the diopside-rich zone of the skarn developed after meta-tonalite. Sample SIT2/1, reflected light. **(b)** Granular textured pyrite (py (gr); alteration ?) with arsenopyrite (asp) inclusions disseminated within the diopside-rich zone of the skarn developed after meta-tonalite. Sample SIT2/1, reflected light. **(c)** Intimate relationship between pyrrhotite (po), chalcopyrite (ccp), pyrite (py), and arsenopyrite (asp) disseminated within the diopside-rich zone of the skarn developed after meta-tonalite. Sample SIT2/1, reflected light. **(d)** Granular textured nucleus (py (gr); alteration ?) of a pyrite-zoned crystal (py), with arsenopyrite (inclusions) disseminated within the diopside-rich zone of the skarn developed after meta-tonalite. Sample SIT2/1, reflected light. **(e)** Chalcopyrite (ccp) associated with pyrite (py), and dispersed pyrrhotite (po) crystals disseminated within the amphibole-rich meta-tonalite. Sample SIT1/Cx26, reflected light. **(f)** Euhedral pyrite (py) crystals in the quartz-calcite vein crosscutting amphibole-rich meta-tonalite. Sample SIT1/Cx26, reflected light. **(g)** Intimate relationship between pyrrhotite (po), chalcopyrite (ccp), and arsenopyrite (asp) disseminated within the quartz-plagioclase-diopside-rich zone of the skarn developed after marble. Sample SIT8/Cx37, reflected light. **(h)** Intimate relationship between pyrrhotite (po) and chalcopyrite (ccp) that occur disseminated within the amphibole-(biotite)-rich zone of the skarn developed after meta-tonalite. Sample EIT17/1, reflected light.

In this study, pyrite of the quartz-calcite vein shows the highest Pb (1,870 ppm) and W (1,420 ppm) concentrations, and a significant abundance of gold (620 ppm). In places, pyrite is actually a cupreous pyrite (*ca.* 17 wt.% of Cu). Cobalt has been detected in the

arsenopyrite (Figure 6), while Se (variable amounts between 96 and 1,000 ppm) occurs widespread in the analysed sulfides, which could be explained by the Se-for-S replacement that likely occurred in this mineral class.



**Figure 6.** Proton miniprobe spectrum of Arsenopyrite (FeAsS; sample SIT8/Cx 37) from the Itajubatiba skarn deposit. Filter: Al 250  $\mu$ m thick; Si K $\alpha$ : detector ionization.

The PIXE results reveal that Au, As, and Ni occur in the pyrrhotite, chalcopyrite, and pyrite (Figure 5), which are disseminated within the

skarns. Silver (< 40 ppm) is mainly present in the chalcopyrite, while W (< 400 to 1,420 ppm) occurs mainly in the pyrite. These results

are proof of the presence of gold linked to the main sulfide phases of the ore-bearing

paragenesis at Itajubatiba.

## CONCLUSIONS

PIXE results reveal that some elements (Mn, Au, As, Bi, Pb, Ni, Co, Se, and W) are found in relatively high concentrations in the sulfides of the Itajubatiba ore. These elements may reflect the geochemical signature of the mineralizing fluids that were involved in the genesis of the Itajubatiba skarn deposit. Pyrite contains the highest amount (690 ppm) of gold discovered in the sulfides, particularly in its granular textured zone, as well as when it occurs in quartz-calcite veins (620 ppm of gold). Granular pyrite appears to be generated by late alteration, as it is also the case of the pyrite filling veins. It is reasonable to assume that late processes, such as remobilisation, taking place in the Itajubatiba ore, are responsible for the genesis of the gold-rich pyrite discovered.

Considering that the pyrite contents in the Itajubatiba skarns vary from 0.5 to 1.0 vol.%, there is 0.75 to 1.5 wt.% of pyrite in these

rocks. These values were obtained by taking into account the modal abundances and the average densities of the main skarn minerals (pyroxene, amphibole, garnet, plagioclase, and pyrite).

For the gold concentrations (200-690 ppm) that were discovered in pyrite from Itajubatiba, one can estimate the gold grade in skarns (considering the gold hosted in pyrite only). It varies from 3.0 to 10.4 ppm for the skarn samples having 1.5 wt.% of pyrite, and from 1.5 to 5.2 ppm for the skarn samples showing 0.75 wt.% of pyrite. These gold grades are economically significant, and could change the exploration perspective of the investigated deposit. The results point to gold related to sulfide phases of the Itajubatiba ore, which contradicts what one could infer from mining reports.

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