OCCURRENCE OF ILVAITE IN THE IGARAPÉ BAHIA Cu-Au DEPOSIT, CARAJÁS PROVINCE, BRAZIL

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ABSTRACT This paper describes the first known occurrence of the mineral ilvaite in Brazil. The mineral is sited in the matrix of magnetite-rich breccias and stockwork veins of the Igarapé Bahia Cu-Au deposit. Electron microprobe analysis (EMPA) of the Igarapé Bahia ilvaite reveals the following composition: $Ca_{0.96}Fe^{2+}_{1.96}Fe^{3+}_{1.00}Si_{2.01}O_8(OH)$ and X-ray diffraction (XRD) data indicate a structure compatible with the monoclinic polymorph (a_0=13.032 Å, b_0=8.810 Å, c_0=5.850 Å and α=90.254°). It is suggested that ilvaite crystallized from hydrothermal solutions, at a temperature range of 300-350°C, under conditions of high high fO_2 and low sulfur activity. The formation of ilvaite is tentatively related to the reaction magnetite + calcite + quartz + H_2O = ilvaite + CO_2 + O_2.

Keywords: ilvaite, Igarapé Bahia, Cu-Au deposit, Carajás

INTRODUCTION Ilvaite was named after its discovery locality, on the Rio Marina, Elba (Latin Ilva) Italy (Blackburn & Dennen 1997). This rare Ca-Fe-silicate occurs typically as a late stage mineral in Ca-Fe-Si-skarns related to the intrusion of granodiorite, quartz diorite, monjograniteand granite (e.g. Shannon 1918, Plimer & Ashley 1978, Gauthier & Albankis 1981, Gole 1981, Kwak 1983, Pesquera & Velasco 1986). Ilvaite also occurs as a product of deuteric or hydrothermal alteration of basalt, dolerite and quartz diorites (e.g. Baker 1953, Naslund 1983, Barton & Van Bergen 1984, Wise & Moller 1990). Less commonly, the mineral is related to low-grade retrometamorphic reactions of ultramafic rocks (Agata & Adachi 1995). Desborough & Amos (1961) report the occurrence of magmatic ilvaite related to the latest stages of gabbro crystallization. This paper describes the mode of occurrence, mineralogical association, chemical composition and crystal structure of ilvaite from the Igarapé Bahia Cu-Au deposit, which is the first reported occurrence of the mineral in Brazil.

GEOLOGICAL SETTING A remarkable feature of the Carajás region is the clustering of a large number of world-class (> 200 Mt) Fe-oxide Cu-Au-(U-REE) deposits (e.g. Salobo, Cristalino, Igarapé Bahia, Sossego) that are collectively known as the Carajás Copper-Gold Belt. The Igarapé Bahia deposit, with total reserves of 219 Mt @ 1.4% Cu and 0.86 g/t Au, is perhaps the best documented deposit of the belt (e.g. Tallarico *et al.* 2000 and references therein).

A low-grade metavolcano-sedimentary sequence (Igarapé Bahia/Grão Pará Group), which includes a variety of volcanic, pyroclastic and epiclastic rocks and minor ironstones, hosts the Igarapé Bahia mineralization. Sandstones that formed in a shallow marine environment (Águas Claras Formation) overlie the former unit. A set of radial fractures and faults control the emplacement of quartz diorite and diabase dikes, which disrupt the metavolcano-sedimentary rocks and the Águas Claras sandstone.

The ore bodies define an ellipsoidal structure at surface and are associated sub-vertical breccia units. The ore-bearing with breccias include fragments of both footwall and hanging wall that are cemented by variable amounts of chlorite, siderite, magnetite, chalcopyrite and minor uraninite and REE-minerals.

OCCURRENCE OF ILVAITE Ilvaite is a rare mineral in the Igarapé Bahia deposit, and was recognized in the matrix of magnetite-rich breccias and veins that crosscut the former. The magnetite breccia include angular fragments (up to 6 cm in diameter) of banded iron formation and altered volcanic rocks. These fragments are welded by a fine-grained isotropic matrix that includes magnetite (8-33%), stilpnomelane (15-40%), chlorite (1-17%), amphibole (5-13%), tourmaline (1-3%), quartz (1-23%), calcite (1-20%), sericite (1-6%) and minor amounts of biotite, apatite, monazite, uraninite, fluorite, epidote and ilvaite. Matrix mineralogy also includes chalcopyrite (1-20%) in equilibrium with bornite (1-6%), and traces of cobaltite. Hessite (Ag_2Te) and native gold particles (3-50μm) occur in the matrix of magnetite breccias as inclusions in gangue minerals, chalcopyrite and bornite.

Stockwork veins, which range from a few millimeters up to 4cm width, crosscut the magnetite breccias. Vein mineralogy includes calcite (40-50%), chalcopyrite (10-30%), magnetite (5-15%), ilvaite (1-10%), quartz (5-10%), fluorite (up to 5%) and tourmaline (up to 5%).

Ilvaite occurs in both breccia matrix and veins as subhedral

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crystals ranging from 50μm to 0.5cm. Ilvaite frequently contains inclusions of magnetite, suggesting that it originated from the alteration of the later. Rare sheelite crystals also occur as inclusions in ilvaite, with hematite commonly occurring as rims on, or filling fractures in ilvaite.

X-RAY CRYSTALLOGRAPHY Ilvaite was examined in a Philips-X'Pert X-ray diffractometer with a θ-θ goniometer. Analytical conditions were: CuKα_1 radiation (graphite monochromator), 40kV accelerating voltage, 55mA current, 5°-75° angular range (2θ), 0.04° step size and 0.5 second/step counting rate. The fifty-four measured X-ray reflections show a very good agreement with the Powder Diffaction File (PDF) - Set 25-149, for monoclinic ilvaite (Table 1). Least-square refinement of the X-ray reflections, assuming monoclinic constrains, yield the following unit cell parameters: a_0 = 13.032 Å, b_0 = 8.810 Å, c_0 = 5.850 Å and α = 90.254°.

Table 1 - X-ray powder diffraction data of ilvaite from Igarapé Bahia.

Igarapé Bahia Ilvaite		PDF 25-149		Igarapé Bahia Ilvaite		PDF 25-149	
d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
7,279	100	7.305	70	1,907	23	1,902	17
6,494	47	6.518	18	1.894	17	1,896	
4,870	8	4,887	10	-	-	1,861	2
4,565	17	4,575	16	-	-	1,848	5
4,169	10	4,172	6	1,855	10	1,846	4
3,889	32	3,984	35	-	-	1,824	3
3.392	8	3,397	14	1,817	5	1,819	3
3,253	45	3,255	55	-	-	1,768	5
-	-	3,237	4	-	-	1,760	5
3,089	14	3,091	18	1,742	14	1,744	20
-	-	3,053	2	1,712	19	1,713	30
2,927	11	2,928	18	1,706	10	1,701	2
2,864	50	2,865	70	1,699	5	1,687	2
2,838	94	2,849	95	1,677	9	1,677	10
-	-	2,840		1,672	28	1,673	13
-	-	2,737	19	-	-	1,671	15
-	-	2,730	20	-	-	1,649	2
-	-	2,721	70	1,631	18	1,633	10
2,713	98	2,714		-	-	1,630	10
2,674	82	2,676	100	-	-	1,624	20
2,614	21	2,617	35	-	-	1,619	20
2,571	14	2,572	20	1.610	52	1,613	10
2,550	16	2,558	19	1,607	34	1,599	8
-	-	2,552		1,575	8	1,578	5
2,495	20	2,496	19	-	-	1,576	
2,436	36	2,438	35	-	-	1,565	5
-	-	2,432		-	-	1,562	6
2,384	11	2,392	25	-	-	1,545	3
-	-	2,385		1,525	21	1,526	22
2,346	16	2,343	30	1,501	16	1,500	35
2,333	23	2,336		1,495	13	1,497	
2,280	4	2,297	3	1.470	24	1,471	20
2,243	1	2,245	5	-	-	1,469	25
2,201	13	2,203	2	1,464	36	1,463	60
2,182	21	2,179	55	-	-	1,458	35
2,169	47	2,171	55	1,426	13	1,426	16
-	-	2,128	10	-	-	1,423	12
-	-	2,121		-	-	1,419	22
2,118	36	2,116	50	-	-	1,415	8
2,108	34	2,109		1,389	5	1,389	4
2,084	18	2.085	20	-	-	1,379	2
1,963	23	1,963	35	-	-	1,376	4
1,956	27	1,953	14	1,366	8	1,366	24
-	-	1,947	17				

Table 2 – Representative microprobe analysis of ilvaite and paragenetic chlorite from magnetite breccias of the Igarapé Bahia Cu-Au deposit.

	Ilvaite (wt%)		Chlorite (wt%)			
	Core	Rim	1	2	3	4
SiO_2	29.02	29.47	24.79	22.94	25.37	25.89
TiO_2	0.08	0.01	0.11	0.04	0.12	0.04
Al_2O_3	0.01	0.00	19.73	15.04	18.86	17.66
$Fe_2O_3^*$	19.50	19.55	0.00	0.00	0.00	0.00
FeO	34.44	34.43	38.78	33.2	36.5	34.18
MgO	0.11	0.10	5.45	5.17	6.61	9.68
CaO	13.73	13.13	0.01	3.42	0.08	1.59
MnO	0.97	1.01	0.15	0.14	0.12	0.09
Na_2O	0.00	0.00	0.30	0.59	0.28	0.20
K_2O	0.00	0.00	0.00	0.00	0.00	0.00
F	0.07	0.00	n.a.	n.a.	n.a.	n.a.
Cl	0.01	0.02	n.a.	n.a.	n.a.	n.a.
H_2O^*	2.16	2.20	10.75	10.67	10.86	10.94
Total	100.11	99.93	100.07	91.21	98.80	100.27
O=F=Cl	0.03	0.00	0.00	0.00	0.00	0.00
Total	100.07	99.92	100.07	91.21	98.80	100.27
# cations per 9 (O,OH)			# cations per 14 (O.OH)			
Si	1.98	2.01	2.76	2.86	2.84	2.83
Ti	0.00	0.00	0.01	0.00	0.01	0.00
Al	0.00	0.00	2.59	2.21	2.49	2.28
Fe^{3+}	1.00	1.00	0,00	0,00	0,00	0,00
Fe^{2+}	1.96	1.96	3.61	3.46	3.42	3.13
Mg	0.01	0.01	0.91	0.96	1.10	1.58
Ca	1.00	0.96	0.00	0.46	0.01	0.19
Mn	0.06	0.06	0.01	0.01	0.01	0.01
Na	0.00	0.00	0.06	0.14	0.06	0.04
K	0.00	0.00	0.00	0.00	0.00	0.00
F	0.02	0.00	-	-	-	-
Cl	0.00	0.00	-	-	-	-
OH	0.98	1.00	7.99	8.00	8.00	8.00
T(°C)**	-	-	336.43	305.70	311.90	314.63

* Fe_2O_3 and H_2O calculated from charge balance
**Chlorite-geothermometer (Cathelineau 1988)
n.a. – not analyzed

MINERAL CHEMISTRY Chemical analyses of minerals were collected on a JEOL-JCXA-733 microprobe, with the following analytical conditions: 15kV accelerating voltage, 15.10^{-9}A current and calibration using natural and synthetic standards. EMPA data of ilvaite reveals a near-stoichiometric composition, $Ca_{0.96}Fe^{2+}_{1.96}Fe^{3+}_{1.00}Si_{2.01}O_8(OH)$, with low manganese content (MnO ~ 1wt%) (Table 2). Chlorite from the matrix of magnetite breccias is typically Fe^{2+}-rich (FeO_t 34-38wt%) and yields, through calculations of the Cathelineau (1988) geothermometer, a temperature range between 305-336°C for the hydrothermal system.

DISCUSSION According to Gustafson (1973), at high fluid pressures, ilvaite is stable below approximately 470°C and over a wide range of fO_2. The mode of occurrence of the Igarapé Bahia ilvaite, together with the temperature estimate given by chlorite-geothermometry, suggests that the mineral formed under hydrothermal conditions at temperatures possibly between 300-350°C. The presence of coexisting magnetite and chalcopyrite in equilibrium with bornite denotes an oxidized and sulfur-poor hydrothermal system. The presence of magnetite inclusions in ilvaite, coupled with the occurrence of paragenetic quartz and calcite, suggest that ilvaite could have formed through the reaction magnetite + calcite + quartz + H_2O = ilvaite + CO_2 + O_2 (Barton and Bergen, 1984). The excess oxygen released from this reaction could be responsible for the precipitation of hematite in fractures, or as rims on ilvaite.

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