PETROGRAPHICAL ASPECTS OF THE SUPERGENE WEATHERING OF GARNET IN THE "SERRA DOS CARAJÁS" (PARÁ, BRASIL).

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ABSTRACT

The copper mineralization of Salobo 3A is associated with a schistose formation in which numerous facies are enriched in almandine garnet. During supergene weathering, the garnet is pseudomorphosed by iron oxi-hydroxides. Three stages are observed: 1- Appearance of a corona of amorphous iron oxi-hydroxides on the walls of the fissures; 2- Formation of a second concentric inner corona of well crystallized goethite; 3- Substitution of the inner garnet residue by cryptocrystalline or amorphous iron oxi-hydroxides. These transformations are isovolumetric with a part of the iron imported. Near the surface, the pseudomorphs of garnet form nodules with a still recognizable boxwork structure.

I. INTRODUCTION

The copper mineralization of Salobo 3A, located about 550 km SSW of Belem (50°W 6°S) in the southeastern part of the Amazonian forest, belongs to the recently discovered mineral province of Carajás. The evaluation work is being carried out by DOGEO (Subcompany of the "Companhia Vale do Rio Doce"). Geological and petrographical studies have shown that copper is associated with a schistose formation in which numerous facies are enriched in garnet (MARTINS et al.,1982). According to these authors, this formation underwent a metamorphism reaching the amphibolite facies, and in some points the granulite facies, followed by a greenschist retrometamorphism.

The weathered cover, about 30m thick, developed at the expense of the schistose formation is being studied. Pits and drillings make it possible to follow the successive stages of garnet weathering, from the parent-rock up to the surface. The climate is characterized by a long wet season (8 to 9 months), an annual rainfall rate of 1 800 mm and an average temperature of 25°C.

Two profiles were sampled from the fresh rock to the surface. These samples were investigated systematically under the polarizing microscope and some were studied with a scanning electron microscope (SEM) and analyzed with a microprobe.

## II. RESULTS

A. The parent material

The mineralogical composition of the parent-rock varies according to the facies but in practically all the facies, amphibole (generally cummingtonite – grunerite type), garnet and biotite occur in variable proportions. According to the facies, magnetite (sometimes very abundant), quartz, olivine and sometimes plagioclase can

be found. The structure of this rock is granoblastic to lepidoblastic with a fine to large grain size (MARTINS et al., 1982). Garnets form irregular porphyroblasts ranging from 1 mm to 2 cm in diameter. Microprobe analyses show that they contain 77 to 82% of almandine (Table 1) and have the following average formula:

$$(Fe^{2+}_{4,89}, Mg_{0,47}, Mn_{0,55}, Ca_{0,15}) \ (Fe^{3+}_{0,12}, Al_{3,88}) \ (Al_{0,17}, Si_{5,83}) \ O_{24}$$
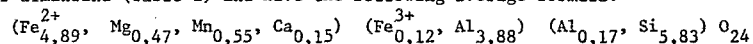
This formula is in accordance with the almandinë composition quoted by DEER et al. (1962). Often, the garnets present a poikiloblastic structure with amphibole or quartz inclusions. Garnets are generally strongly fractured (Fig. 1.1). In numerous fissures and at the grain edges, chlorite and green biotite (Plate 1.a), originating from the retrometamorphism phases, is observed.

Table 1: Microprobe and mineralogical analyses of six garnet grains.

Chemical composition (%)

	1	2	3	4	5	6
SiO2	35,58	35,13	34,78	34,84	35,76	35,29
Al2O3	20,87	21,00	20,94	20,57	20,71	20,57
FeO	36,90	36,23	35,59	35,88	37,07	36,15
MnO	3,35	3,44	4,28	4,79	3,62	3,54
MgO	2,05	2,36	2,05	1,70	1,62	1,46
CaO	1,21	1,55	1,68	1,64	1,23	1,29
	99,96	99,71	99,32	99,42	100,01	98,30

Number of ions on the basis of 24 (O,OH)

	1		2		3		4		5		6	
Si	5,852	6	5,790	6	5,770	6	5,800	6	5,888	6	5,900	6
Al	0,148		0,210		0,230		0,200		0,112		0,100	
Al	3,889	4	3,862	4	3,857	4	3,828	4	3,900	4	3,945	4
Fe3+	0,111		0,138		0,143		0,172		0,100		0,055	
Fe2+	4,946		4,838		4,776		4,803		4,987		4,981	
Mg	0,505	6,12	0,584	6,17	0,511	6,19	0,424	6,19	0,399	6,11	0,365	6,08
Mn	0,460		0,479		0,600		0,674		0,504		0,499	
Ca	0,213		0,273		0,299		0,293		0,216		0,230	

Mol. % end members

	1	2	3	4	5	6
Almandin	80,7	78,4	77,2	77,6	81,7	82,0
Andradite	2,8	3,5	3,6	4,3	2,5	1,4
Grossular	0,7	0,9	1,2	0,4	1,0	2,4
Pyrope	8,2	9,5	8,3	6,8	6,5	6,0
Spessartite	7,6	7,7	9,7	10,9	8,3	8,2

B. Initial stages of garnet weathering

Garnet weathering starts early, namely simultaneously with the amphibole weathering. In the first weathering stage, a fine dark corona of iron oxi-hydroxides, with an amorphous aspect, appears at the walls of chlorite fissures. The iron oxi-hydroxides also penetrate the garnet fractures, giving rise to a garnet mosaic (Fig. 1.2).

In the next stage, a second corona of well crystallized goethite forms according to a centripetal pattern at the expense of the garnet (Plate 1.b; Fig. 1.3); these crystallizations develop on intramineral fissures and contact surfaces between the garnet and its inclusions (quartz for example). EMBRECHTS and STOOPS (1982) described the same type of weathering for garnets of Cameroon. In our case, however, the formation of well crystallized goethite takes place earlier. Indeed, this stage is reached at a maximum of 5 meters from the fresh rock and biotites are still in

their first stage of weathering. In this stage, the weathering of the fissural chlorites into smectite begins, even as the iron segregation in the biotites and in the amphiboles. Our observations differ from those of SARAZIN et al. (1982) who observed also in Cameroon, a garnet pseudomorph consisting of amorphous or poorly crystallized iron oxi-hydroxides; well crystallized goethite appears only later, at the expense of these amorphous oxi-hydroxides.

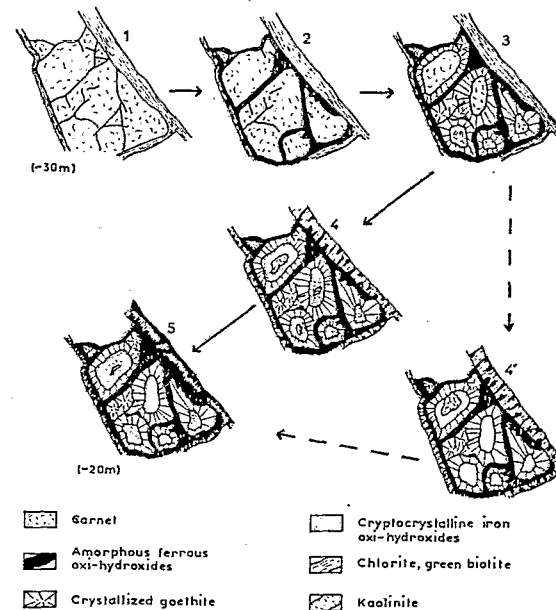|	
Garnet	Cryptocrystalline iron oxi-hydroxides
Amorphous ferrous oxi-hydroxides	Chlorite, green biotite
Crystallized goethite	Kaolinite

Fig. 1 : Schematic representation of garnet weathering

C. Subsequent stages of garnet weathering

Two evolutions, which seem independent of the facies, can be observed.

In the first case, which is rare, one observes a congruent dissolution of the garnet nucleus: a boxwork structure is formed (Plates 1.c and 2.a). In the boxwork cavities, gibbsite or goethite crystallites may appear, but more frequently, these cavities are filled by amorphous or poorly crystallized iron oxi-hydroxides (Plate 1.d; Fig. 1.4). This weathering evolution is in agreement with the observations of EMBRECHTS and STOOPS (1982) in Cameroon.

In the second case, which is more frequent, a second corona of iron oxi-hydroxides appears between the well crystallized goethite and the garnet nucleus. Under the optical microscope, this material seems amorphous or poorly crystallized (Plate 1.c). SEM observation shows that it consists of cryptocrystalline iron oxi-hydroxide (Plate 2.b). This second corona increases in a centripetal pattern at the expense of the garnet, to fill completely, or nearly completely, the volume initially occupied by the silicate (Plate 1.f). SEM observation shows that the porosity is more and more important from periphery to center (Plate 2.c; Fig. 1.5). At this stage, the phyllosilicates weathering is more advanced.

In fissures, chlorites are nearly completely transformed into smectite and kao-

linite. As for biotite, the iron segregation phase is more advanced and one observes the beginning of its exfoliation. Amphiboles are completely transformed into iron oxi-hydroxides and into smectite. Once more, the rapidity of the garnet weathering is shown, since only 10 meters above the fresh rock no residual garnet is present. There is pseudomorphose of the garnet by iron oxi-hydroxides. Structures that have been formed remain stable up to the top of the profile,where they become rounded and form iron nodules. In these nodules, typical structure described above is still re-cognizable, although the well crystallized goethite shows a less massive aspect (see plate 2.d). In the superficial horizons, we never find the boxwork structure with central voids. Therefore one supposes that the voids are filled by iron oxi-hydroxi-des as described by EMBRECHTS and STOOPS (1982).

Table 2: Microprobe analyses of goethite end iron oxi-hydroxides (%)

	Ext 7	Med 8	Med 9	Med10	Med11	Int12	Int13	Int14
Fe_2O_3	75.58	76,16	74.33	75.13	71.88	73.85	72.09	69.25
Al_2O_3	6.80	6.58	6.04	6.96	7.25	8.97	7.62	6.80
SiO_2	3.93	3.56	3.80	4.00	3.36	6.53	3.53	4.70
TiO_2	0.00	0.00	0.00	0.00	0.15	0.00	0.00	0.00
MgO	0.00	0.00	0.00	0.00	0.27	0.00	0.27	0.00
Σ	86,31	86,29	84.17	86.09	82.91	89.35	83.51	80.75
H_2O	13.69	13.71	15.83	13.91	17.09	10.65	16.49	19.25

Ext = External amorphous corona
Med = Medium corona of well crystallized goethite
Int = Internal poorly crystallized iron oxi-hydroxides
H_2O = Values are calculated by difference
(eventually including P and Cu)

Microprobe analyses of different iron oxi-hydroxide coronas do not show impor-tant chemical differences (Table 2). Indepedently of their position and their degree of crystallization, coronas present concentrations of about 7% Al_2O_3, 4% SiO_2 and 73% Fe_2O_3. The spectre obtained with the microprobe shows also trace of copper even as a poorly defined pick which may be due to phosphorus. Its origin may be apatite present in these formations. The phosphorus fixation by iron oxi-hydroxides is des-cribed by numerous authors (CABRERA et al., 1977; RUSSEL et al., 1974).

III. DISCUSSION AND CONCLUSION

All the transformations described are isovolumetric (Fig. 1). Knowing the ave-rage concentrations of elements in garnet and in goethite, and using a minimum den-sity for these minerals, we can calculate the percentage of gain and loss for each element during the garnet weathering as follows:

$$D = \frac{P_{go} - P_{gr}}{P_{gr}} \times 100 \quad ; \quad as \ p = \frac{P.C}{100} \ and \ P = V.d \ : \ p = \frac{V.d.C}{100}.$$

As the transformations are isovolumetric, $V_{gr} = V_{go}$, and the formula can be writed:

$$D = \frac{d_{go}.C_{go} - d_{gr}.C_{gr}}{d_{gr}.C_{gr}} \times 100$$

where:
D = percentage of gain (+) and loss (-) ;
p = weight of element in mineral goethite (p_{go}) and garnet (p_{gr}) ;
P = weight of mineral
V = volume of mineral goethite (V_{go}) and garnet (V_{gr}) ;
C = concentration (%) of element in mineral goethite (C_{go}) and garnet (C_{gr}) ;
d = density of mineral goethite (d_{go}) and garnet (d_{gr}).

If we take a minimum density of 3.3 for goethite and 4.3 for garnet (FISCHESSER 1970), we find that the garnet does not contain enough iron to form the same volume of goethite (Table 3).

Table 3: Estimation of the gain and loss of elements during the isovolumetric garnet weathering in V%.

	C_{gr}	D_{go}	P_{gr}	P_{go}	D
Fe	28,22	51,33	1,21	1,69	+ 39,67
Al	11,00	3,77	0,44	0,12	- 74,47
Si	16,44	1,95	0,71	0,06	- 91,55

D = percentage of gain (+) and loss (-);

$C_{gr,go}$ = average concentration of element in garnet and goethite;

$P_{gr,go}$ = weight of element by unit volume in garnet and goethite (garnet density = 4.3; goethite density = 3.3).

As voids do not appear between the garnet and the goethite, we can estimate that, relative to the garnet iron, a minimum of 39% of the iron is imported. As for the inner filling of iron oxi-hydroxide, we obtain a density of 2,36, if we consider that only garnet-iron has contributed to its formation. This value would seem to be reasonable for the significantly porous cryptocrystalline goethite observed in the center of the boxwork cells (Plate 2.d). However, the presence of copper and phos-phorus in the iron oxi-hydroxides suggests the possibility of an external source, at least for these elements.

In this paper we show that garnet weathers very quickly into iron oxi-hydro-xides. Two evolutionary pathways are observed: pseudomorphose of the garnet by iron-oxi-hydroxides and congruent dissolution of the garnet with formation of a boxwork structure. In both cases the transformations occur at constant volume with external contribution of iron probably coming first from amphiboles and later from biotites.

AKNOWLEDGMENTS

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RÉSUMÉ

La minéralisation cuprifère de Salobo 3A est associée à une formation schisteuse dont de nombreux faciès sont riches en grenat almandin. Lors de l'altération superficielle, le grenat est pseudomorphosé en oxy-hydroxydes de fer. Trois étapes ont été observées: 1- Apparition d'une couronne d'hydroxydes de fer amorphes au contact des fissures périphériques ou internes; 2- Formation d'une seconde couronne, interne à la première, de goethite bien cristallisée; 3- Remplacement des résidus internes de grenat par des hydroxydes de fer cryptocristallins ou amorphes. Ces transformations sont isovolumétriques avec importation d'une partie du fer. Près de la surface les pseudomorphoses de grenat forment des nodules dont la structure interne cloisonnée, est encore reconnaissable.
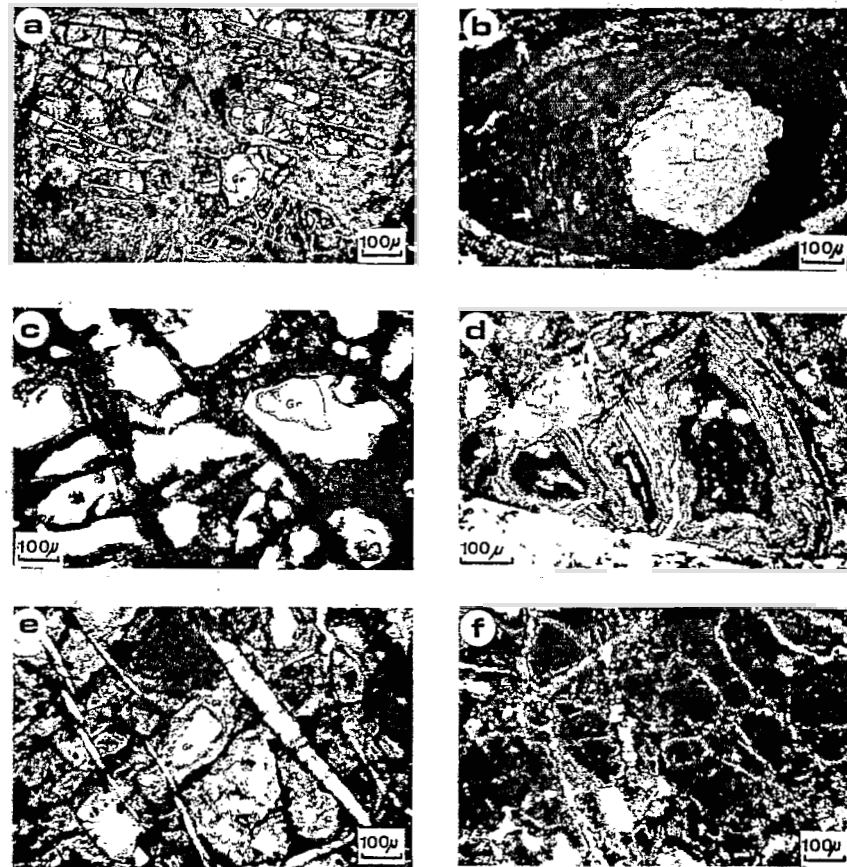
PLATE I : THIN SECTION MICROGRAPHS.

a : Unweathered garnet with chloritic fissures. - plain light.

b : Well crystallized goethite surrounding a garnet nucleus. Note the garnet relic in the goethtite. - plain light.

c : Boxwork structure of goethite with a garnet remnant (Gr) in the void. Note the amorphous corona and the inner well crystallized goethite. - plain light.

d : Infilling structure formed by amorphous or poorly crystallized iron oxi-hydroxides. - plain light.

e : Weathered garnet. Note the poorly crystallized corona (In) that appears between the well crystallized goethite (Go) and the garnet (Gr). In the fissure, chlorite is weathered into smectite. - plain light.

f : Completely weathered garnets into well crystallized goethite (clear peripheral coronas) and dark brown cryptocrystalline iron hydroxides cores. - plain light.
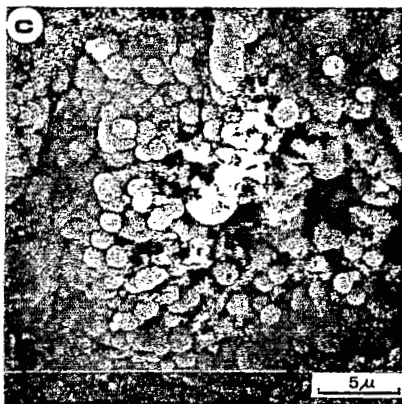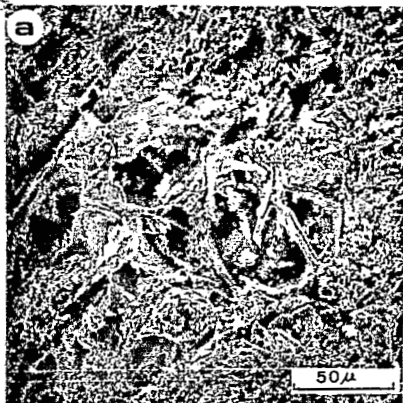
PLATE II : SEM PHOTOGRAPHS.

a : Goethite boxwork structure. Note the twin layers of iron hydroxide on both sides
    of the original fissural network and the open internal cavities.

b : Formation of cryptocrystalline iron oxi-hydroxides (IN) between well crystalli-
    zed goethite (GO) and garnet (GR).

c : Completely weathered garnet. Note the increasing porosity from periphery to
    center.

d : Completely weathered garnet (sample near the surface). Note the less massive as-
    pect of the well crystallized goethite (GO).