

## MINERALOGICAL EVOLUTION OF SUPERGENIC ALTERATION IN ALKALINE ROCKS OF LAGES, SOUTHERN BRAZIL

Milton L.L. FORMOSO\*, Norberto DANI\*, André NOVIKOFF\*\* and Ida VALETON\*\*

**ABSTRACT** - The District of Lages (SC Brazil) is the southernmost known bauxite deposit of Brazil. Mineralogical and chemical changes of phonolites show that nepheline is the first mineral to change, releasing sodium first and potassium and silicon later. The alteration of nepheline forms dissolution cavities which highly increase rock porosity. In some cases gibbsite partially or entirely fills the cavities. Globular material is found side by side with large crystals of gibbsite on the corroded K-feldspar. The advanced alteration of feldspar converges to gibbsite in the final stage but locally shows an intermediate silico-aluminous phase. Pyroxenes are altered to goethite along the cleavage and parting planes at first and are almost completely replaced in more advanced stages of alteration. Later veinlets of white halloysite and lithiophorite run across the entire weathering profile.

### INTRODUCTION

The southernmost bauxite deposit ever described in Brazil is found in the Lages Alkaline District ( $\phi = 27^{\circ}33'S$ ,  $\lambda = 50^{\circ}13'W$ ), made up of Upper Cretaceous rocks (AMARAL et al. 1966; SCHEIBE et al., 1985) of volcanic and subvolcanic alkaline intrusions in the Parana Basin sequence.

Among the alkaline rocks, phonolites are dominant and the bauxite deposits are related to this type of rock by virtue of its susceptibility to weathering and high aluminium and low iron contents. Although the bauxite is a weathering product restricted to alkaline rocks, recent papers (SZUBERT and VERGARA, 1975; DANI, 1988) have shown evidence that the laterization processes have extended to other rocks such as the diabases and basalts of the Parana Basin.

The Lages bauxite shows much evidence of being a paleodeposit. Lages is geographically situated on the limit of the favourable zone (LELONG et al, 1976; BARDOSSY, 1982) for bauxite formation (altitude of 900m and temperate climate) and podzolization instead of lateritization is the present dominant process and the presence of halloysite in the external positions of the weathered blocks might represent an equilibrium with the present weathering conditions. The preservation of bauxite deposits is related to the local geomorphological positions where erosion is less accentuated (Serra da Farinha Seca-Lages).

- 
- \* Instituto de Geociências - UFRGS - 9500 Av. Bento Gonçalves - 91500. Porto Alegre (Brazil).
  - \*\* ORSTOM, 1 Rue Blessig, 67084 Strasbourg - France.
  - \*\*\* Geologisch-Palaontologisches Institut - Bundestrasse 55 - Hamburg 2000 - Germany

## MATERIALS AND METHODS

The phonolites of the Lages area have a quite similar chemical composition, with a dominant mineralogy comprised of K-Feldspar (orthoclase), nepheline and pyroxenes of the diopside-hedenbergite series (salite) and aegirine-augite.

A general profile is difficult to present because of local variations, but in the studied area would have an average thickness of 10 meters divided into alteration zones, each one characterized by its structure, mineralogical and chemical composition and also by different properties such as colour, cohesion and density (fig.1). The alteration facies are named from the base to the top of profile: fresh/alterated rock; lower clayey horizon; bauxitic zone; upper clayey horizon and recent humic soil. In general, the structure and organization of the rock are preserved, constituting an isalterite. In the upper clayey horizon, collapse structures and evidence of pedological activity (aloterite) are found.

Sampling material was collected in soilpits located according to the toposequences (fig.2); samples were taken every one meter between the fresh, unweathered rock and the soil's surface.

Besides, detailed profile observations were made in quarries and outcrops; undisturbed samples were taken for determination of physical properties and for the study of micromorphological and geochemical aspects.

X-Ray diffraction and chemical analyses of major and minor elements were performed on all samples. Scanning Electron Microscopy (Cenpes Laboratory, Petrobras, Brazil) with a Hitachi equipment and Electron Probe Analysis (Camebax, University of Nancy, France) were carried out on selected samples.

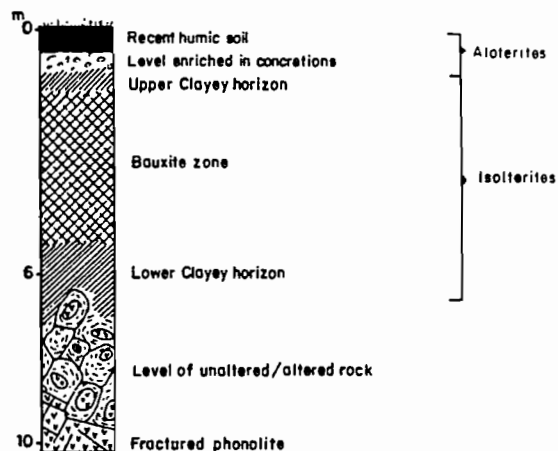


Figure 1: Typical weathering profile (complete) of Serra da Farinha Seca.

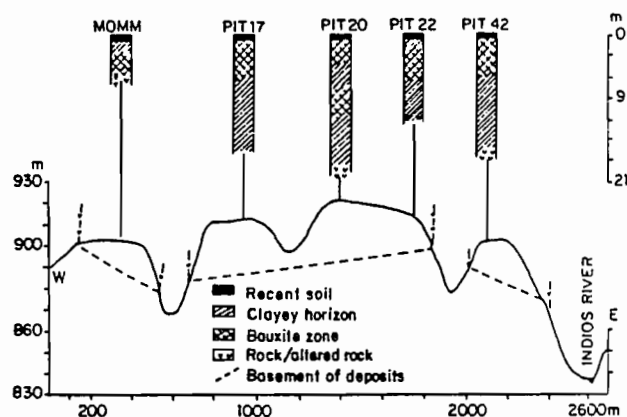


Figure 2: An East-Western toposequences in Farinha Seca.

## RESULTS AND DISCUSSION

## A - CHARACTERISTICS OF THE ALTERITE

Only a restricted proportion of primary minerals tend to remain in the alterite whose mineralogy comprises mainly gibbsite, 10Å halloysite and aluminous goethite besides very small quantities of boehmite. Gibbsite dominates in bauxite zone and 10Å halloysite in the clayey horizon (fig.3).

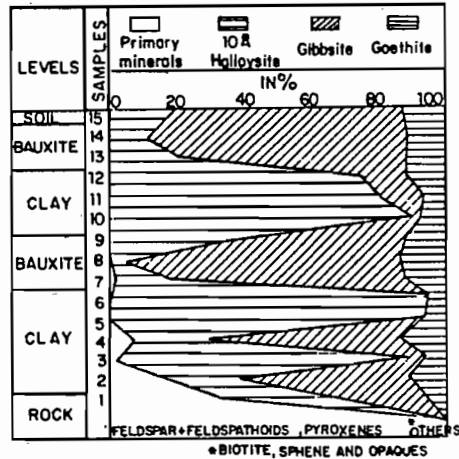


Figure 3: Detailed mineralogical distribution in the soilpit number 20.

The principal physical and chemical properties of the alteration facies are displayed in table 1. In the fresh rock, average values of 2% for porosity and 2.3 for density are found whereas in the bauxite zone, the density approaches unity and porosity attains 60%, related to a large quantity of dissolution of primary minerals.

The alteration facies may be represented, from a chemical viewpoint, by an alteration index, similar to that adopted by SCHELLMANN (1981), which adapted to the weathering conditions in Lages, describes the mobility of chemical elements:

$$i' = (Al_2O_3 + Fe_2O_{3\text{tot.}}) \times 100 / (SiO_2 + Na_2O + K_2O)$$

Within a 95% statistical confidence limit, the alteration zones show the following values:

Fresh/altered rock:  $i' < 80$

Lower and upper clayey horizon:  $i'$  from 80 to 200.

Bauxite zone:  $i' > 200$ .

East-western toposequences (fig.2) in the typical area of bauxite deposits (Farinha Seca) display the principal characteristics of those deposits, showing bauxitic and clayey horizons, the latter ones occupying mainly the base of the profiles. The bauxite deposits cap the main high places but are deeply incised by the present drainage, showing that they are in disequilibrium with the recent environment conditions.

Table 1 : Average chemical composition in weathering profiles developed in phonolites in the area of Farinha Seca

	fresh fonolite	Weathered rock level	Clay horizon	Bauxite zone
Major elements (%)				
SiO <sub>2</sub>	53.69	47.00	37.80	10.20
Al <sub>2</sub> O <sub>3</sub>	21.61	27.00	37.10	53.00
Fe <sub>2</sub> O <sub>3</sub> tot.	3.50	3.50	4.40	6.80
MgO	0.57	0.21	0.02	--
MnO	0.20	0.18	0.25	0.15
CaO	1.13	0.90	0.03	0.01
Na <sub>2</sub> O	9.97	4.20	--	--
K <sub>2</sub> O	5.16	4.80	0.60	0.20
TiO <sub>2</sub>	0.31	0.37	0.50	0.80
P <sub>2</sub> O <sub>5</sub>	0.03	0.05	0.08	0.14
H <sub>2</sub> O +	3.41	7.30	15.40	27.70
H <sub>2</sub> O -	0.52	4.00	3.40	0.90
Total	100.10	99.51	99.58	99.90
Porosity (%)				
	2.0	14.0	50.0	60.0
Density (d)				
	2.3	2.0	1.5	1.1
i	2.14	1.54	0.91	0.17
i'	37	55	108	575
Obs.: $i = \text{SiO}_2 / (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ - weathering index as defined by SCHELLMANN (1981).				
$i' = (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \text{ tot}) \times 100 / (\text{SiO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O})$ - weathering index employed in this work.				
* bulk density measured in samples dried in the air.				

## B - MINERALOGICAL EVOLUTION OF THE ROCK

## 1. Nepheline

Nepheline is the first mineral to be attacked during weathering, starting from discontinuities and mineral outlines. It evolves to a primary plasma formed by gibbsite with large losses of mass, involving dissolution cavities that increase secondary porosity and display an alveolar fabric (fig.4).

Besides Si, Al and Na, nepheline contains Fe and K. Nepheline analyses, in various stages of alteration (tab.2), show that the mobility of sodium is higher than that of potassium. The beginning of nepheline alteration, occurring along the fracture planes or borders, forms an amorphous material with excess of alumina (ion ratio Si/Al=0.70) (tab. 3). In the zones of more advanced alteration, gibbsite, which is the final product of alteration, is associated with amorphous material (tab.3).

## 2. Pyroxenes

Aegerine-augite is the dominant phase, showing a large variation in composition but also a tendency to have a central zone richer in calcium, magnesium and manganese, with

more sodic borders.

At the first stage of alteration, (fig.5) pyroxenes, besides exhibiting corrosion features are replaced by a primary plasma of goethite and ferruginous or silico-ferruginous amorphous material. A type of globular goethite which replaces pseudomorphically the pyroxene grows parallel to the "C" axis of the mineral and attains an average diameter of 5Å. Another type of goethite, better crystallized, grows normal to the fracture and parting walls. Using X-Ray diffraction, 110 and 111 reflections (SCHULZE, 1984), for estimation of aluminium in goethite, show values between 20 to 25% aluminium.

In the final stage of alteration, pyroxenes are entirely replaced by a primary plasma of goethite and by the transfer plasma of gibbsite which occupies the dissolution

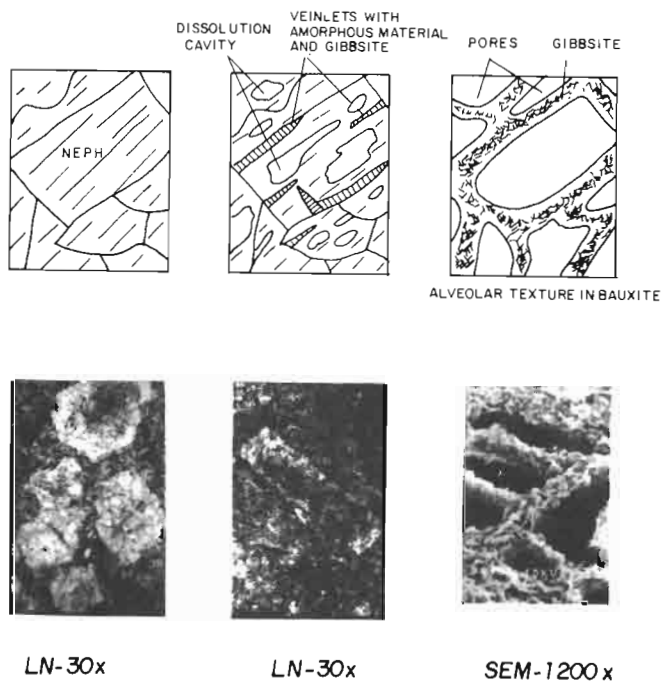


Figure 4: Schematic evolution of weathering of nepheline

cavities. If aluminium is taken as constant, the enrichment of this element would be shown by the loss of all other elements (tab.4) but this would disagree with micromorphological and geochemical observations that iron and titanium are concentrated. Confirming this viewpoint, the isoiron and isotitanium are better indices of relative gains and losses than isoaluminium one, as they show constancy of iron and titanium and a large gain of aluminium.

Tab. 2 - Chemical analyses of nepheline in different stages of alteration

Oxide	oxide in %			concentration ratio in % isoaluminium method	
	1	2	3	1 → 2	1 → 3
SiO <sub>2</sub>	44.98	41.67	30.95	-1	- 45
Al <sub>2</sub> O <sub>3</sub>	32.71	30.67	41.19	0	0
Fe <sub>2</sub> O <sub>3</sub>	0.66	0.63	0.97	+ 2	+ 17
K <sub>2</sub> O	5.21	4.79	0.08	- 2	- 99
Na <sub>2</sub> O	15.61	12.51	0.04	-15	-100
Total	99.17	90.27	73.23	1-Unaltered nepheline	
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	2.34	2.31	1.28	2-Altered nepheline (stage I)	
Na <sub>2</sub> O/K <sub>2</sub> O	4.54	3.96	0.83	3-Altered nepheline (stage II)	

Tab. 3 - Chemical analyses of nepheline and associated alteration products

Oxides	Oxides in %			Ions	Number per formula		
	1	2	3		1 (4 O)	2 (5 O, 4 OH)	3 (3 OH)
SiO <sub>2</sub>	42.34	34.29	2.91	Si	1.06	1.68	0.03
Al <sub>2</sub> O <sub>3</sub>	31.75	41.43	77.44	Al	0.93	2.39	0.95
Fe <sub>2</sub> O <sub>3</sub>	0.63	0.74	1.04	Fe	0.01	0.03	0.01
TiO <sub>2</sub>	0.00	0.02	0.00	Ti	0.00	0.00	0.00
CaO	0.23	0.01	0.00	Ca	0.01	0.00	0.00
MgO	0.00	0.01	0.00	Mg	0.00	0.00	0.00
K <sub>2</sub> O	5.29	0.13	0.00	K	0.22	0.01	0.00
Na <sub>2</sub> O	14.51	0.10	0.01	Na	0.70	0.01	0.00
Total	94.75	76.73	81.41	Si/Al	1.14	0.70	0.03

1-Nepheline 2-Amorphous fissural material 3-Gibbsitic fissural material

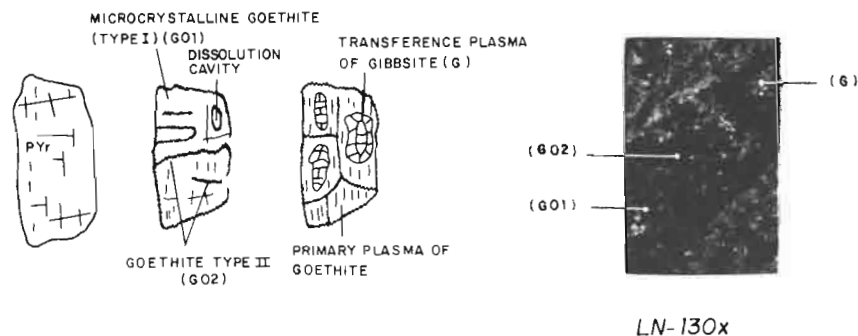


Figure 5: Schematic evolution of weathering of aegirine-augite

Tab. 4 - Chemical analyses of pyroxenes in different alteration stages

Oxides	oxides in %			ratio of concentration (%)					
	1	2	3	Isoaluminium method		Isoiron method		Isotitanium method	
				1→2	1→3	1→2	1→3	1→2	1→3
SiO <sub>2</sub>	52.11	13.53	5.25	-89	-100	-80	-94	-71	-93
Al <sub>2</sub> O <sub>3</sub>	0.53	12.45	22.74	0	0	+1731	+2484	+2123	+2815
Fe <sub>2</sub> O <sub>3</sub>	24.54	31.43	40.61	-95	-96	0	0	+21	+13
TiO <sub>2</sub>	0.51	0.54	0.75	-95	-97	-17	-11	0	0
CaO	5.57	2.33	0.31	-98	-100	-67	-97	-61	-96
MgO	0.37	0.07	0.07	-99	-100	-85	-89	-82	-87
K <sub>2</sub> O	0.03	0.00	0.00	-100	-100	-100	-100	-100	-100
Na <sub>2</sub> O	10.32	1.44	1.60	-99	-100	-89	-91	-87	-89
Total	93.98	61.65	71.33						
Fe <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	29.72	1.61	1.14	1 - Unaltered aegirine-augite					
SiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	5.66	1.15	0.35	2, 3 - Altered aegirine-augite					

### 3. Feldspars

The feldspars (orthoclase) are the most common minerals in the phonolites and represent the phase richest in potassium. At the beginning of the process, the feldspar is corroded and with deeper alteration loose particles appear on the surface of the feldspar with kaolinitic composition (Si/Al ion ratio equal 1), concentrated along the intramineral fractures or crystallographic orientations. At this first stage, under the SEM, globular particles are seen which may be 10Å halloysite or amorphous material (fig.6). At a later stage, stronger corrosion of feldspars forms large dissolution cavities in which remobilized materials of the primary plasma are deposited. In the clayey horizons, the dominant primary plasma is halloysite, which replaces the feldspar, while in the bauxite zone, it is gibbsite. Even in the bauxite zone, amorphous materials of silico-aluminous compositions occur (tab. 5) which are taken as an intermediate phases. These may evolve to gibbsite or halloysite depending on local geochemical conditions. The content of available silica in the microsystem and local waterdrainage/permeability parameters would determine the type of final alteration (ferralitic or sialitic), perhaps explaining the sequence of bauxitic and clayey horizons in the alteration profile.

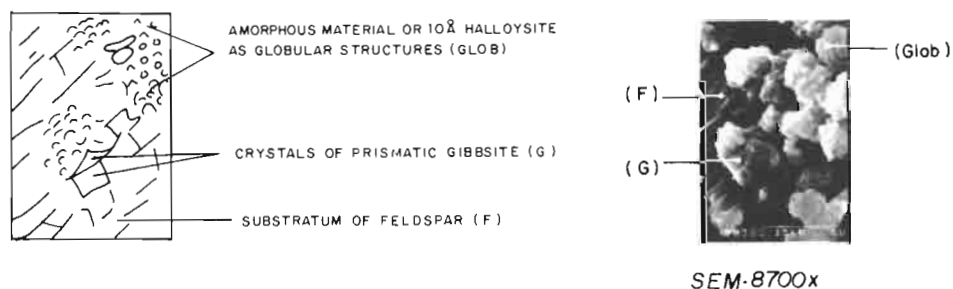


Figure 6: Globular structures and gibbsite growing in feldspar substratum

Tab. 5 - Chemical analyses of feldspar and primary alteration plasma

Oxides	oxides in %			ions per formula		
	1	2	3	1 (8 O)	2 (5 O, 4 OH)	3
SiO <sub>2</sub>	64.71	38.51	33.86	2.95	1.74	1.73
Al <sub>2</sub> O <sub>3</sub>	17.97	43.69	39.03	0.97	2.33	2.35
Fe <sub>2</sub> O <sub>3</sub>	0.10	0.18	0.24	0.00	0.01	0.01
K <sub>2</sub> O	15.75	0.06	0.07	1.20	0.00	0.00
Na <sub>2</sub> O	0.77	0.03	0.02	0.07	0.00	0.00
Total	99.30	82.47	73.22	1 - Unaltered feldspar		
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	6.12	1.52	1.48	2,3 - Plasma of alteration		

## C. INTERNAL REORGANIZATION

Later mobilization along fractures through the entire profile is very common. 10Å halloysite and lithiophorite deposit in the fracture system, occupying the zone of higher circulation and also in pores or holes caused by dissolution of primary minerals. The deposition of these minerals is related to later processes which indicate the instability of normal paragenesis associated with the bauxite. Among various manganese oxides, lithiophorite is the most important. The presence of nuclei of gibbsite is essential for the formation of lithiophorite, since both have a similar structure according to CHUKHROV et al. (1982). Lithiophorite is enriched in Ce (very high values), Zr and Nb (tab. 6).

The remobilization of aluminium is very common in the profile. Cutans of gibbsite, gibbsite veinlets, gibbsite nodules and tubes, large crystals of gibbsite in the filling of pores all occur. This remobilization is later and probably associated with the formation of aluminium chelates (VIOLANTE and VIOLANTE, 1980) with further precipitation of gibbsite.

Tab. 6 - Chemical analyses of lithiophorites associated with manganese veins

Oxides	oxides in %			ions number per formula		
	1	2	3	1	2	3
SiO <sub>2</sub>	0.11	0.25	0.93	0.001	0.003	0.014
Al <sub>2</sub> O <sub>3</sub>	24.79	25.43	3.61	0.336	0.342	0.065
Fe <sub>2</sub> O <sub>3</sub>	0.98	0.39	0.06	0.008	0.003	0.001
TiO <sub>2</sub>	0.17	0.06	0.56	0.001	0.001	0.006
CaO	0.00	0.08	0.60	0.000	0.001	0.010
MgO	0.01	0.04	0.46	0.000	0.001	0.011
K <sub>2</sub> O	0.11	0.01	0.95	0.002	0.000	0.003
Na <sub>2</sub> O	0.04	0.07	0.11	0.001	0.002	0.028
MnO	45.50	45.59	60.69	0.443	0.441	0.790
Nb <sub>2</sub> O <sub>5</sub>	0.00	0.15	0.13	0.000	0.001	0.001
Ce <sub>2</sub> O <sub>3</sub>	0.04	0.12	3.62	0.000	0.000	0.012
ZrO <sub>2</sub>	2.86	2.57	0.05	0.016	0.014	0.000
Total	74.61	74.76	71.77	Considering 2(OH)		



## CONCLUSIONS

1. Field and micromorphological observations enable characterization of the bauxite deposits as residual with dominant relict fabric with the pores and larger empty spaces related mainly to the dissolution of nepheline, orthoclase and pyroxenes.
2. Nepheline tends to be altered at the first stages which is showed by the loss of sodium in nepheline grains and even in the entire profile.
3. Feldspars and pyroxenes are more resistant to supergenic alteration and the feldspars show a dual behaviour which, depending on the local microsystem, leads to 10Å halloysite or directly to gibbsite. Intermediate amorphous phases with various SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio are also formed. Pyroxenes have altered to goethite and gibbsite.
4. Later veinlets of 10Å halloysite and lithiophorite cut across the entire profile, probably representing a later phase of the weathering process.
5. The present temperate climate of Lages is more adequate for podzolization processes than lateritization and the presence of halloysite in the external positions of weathered blocks might represent an equilibrium with the present weathering conditions.

ACKNOWLEDGMENTS - A Brazilian-German joint project between the Universities of Hamburg, São Paulo, and Rio Grande do Sul on bauxite genesis is presently sponsored by BMFT, Bonn, and CNPq, Brazil. Special thanks are addressed to A. J. Melfi who stimulated this project and ORSTOM for the laboratory facilities.

## REFERENCES

- AMARAL G., CORDANI U. G., KAWASHITA K. and REYNOLDS J. H. (1966) - Potassium-argon dates of basaltic rocks from Southern Brazil. *Geochimica Cosmochimica Acta*. Oxford, 30:159-189.
- BARDOSSY G. (1982) - A comparison of the main lateritic bauxite regions of our globe. In: International Seminar on Lateritisation Processes, 2., São Paulo, *Proceedings*, p. 15-51.
- CHUKHROV F. V., GORSHKOV A. I., SIVTSOV A. V. and BARESOVSKAYA V. V. (1982) - On the manganese mineralogy in the lateritic weathering crusts of ultrabasic rocks. In: International Seminar on Lateritisation Processes, 2., São Paulo, *Proceedings*, p. 147-58.
- DANI N. (1988) - *Alteracao supergenica de rochas alcalinas na regio de Lages, Santa Catarina - Formacao de bauxita*. Curso de Pós-Graduação em Geociências-Dissertação de Mestrado, Porto Alegre, RS, Brazil.
- LELONG F., TARDY Y., GRANDIN G., TRESCASES J. J. and BOULANGE B. (1976) - Pedogenesis, chemical weathering and processes of formation of some supergene ore deposits. In: *Handbook of estrata-bound and stratiform ore deposits*. Amsterdam, Elsevier, v. 3, p. 93-173.
- SCHEIBE L. F., KAWASHITA K. and GOMES C. B. (1985) - Contribuição a geocronologia do complexo alcalino de Lages, SC. In: SIMPÓSIO SUL BRASILEIRO GEOLOGIA, 2., Florianópolis, *Anais...*, Florianópolis, SBG, p. 299-307.
- SHELLMANN W. (1981) - Considerations on the definition and classification of laterites. *Proc. int. sem. lat. processes*, India, p. 1-10.
- SCHULZE D. G. (1984) - The influence of aluminum on iron oxides. VIII-Unit-cell dimensions of Al-substituted goethites and estimation of Al from them. *Clays and Clay Minerals*. Clarkson, 32(1):36-44.
- SZUBERT E. C. and VERGARA V. D'AVILA (1975) - *Avaliacao das reservas e da qualidade dos depositos de bauxita do municipio de Lages, SC*, Porto Alegre, SUDESUL-CPRM. 68p.
- VIOLANTE A. and VIOLANTE P. (1980) - Influence of pH concentration and chelating power of organic anions on the synthesis of aluminium hydroxides and oxyhydroxides. *Clays and Clay Minerals*. Clarkson, 28(6):425-34.

# SCIENCES GÉOLOGIQUES

Proceedings of the 9<sup>th</sup> International Clay Conference  
Strasbourg, 1989

Volume I

CLAY-ORGANIC INTERACTIONS  
CLAY MINERALS IN SOILS

Editors in chief

V.C. FARMER and Y. TARDY

Associate Editors : R.A. EGGLETON, B. FRITZ, R. GIESE, K. KODAMA, H. PAQUET,  
J.A. RAUSSEL-COLOM and R.J. WILSON

Editing coordination : J. DUPLAY

## COMITÉ D'ÉDITION

---

Directeur de la publication et Rédacteur en chef : Bertrand FRITZ  
Rédactrices en chef adjointes : Hélène PAQUET et Anne-Marie KARPOFF  
Secrétaire de rédaction : Danièle AUNIS  
Responsable de l'impression : François GAUTHIER-LAFAYE  
Responsable de la gestion financière : Bertrand FRITZ  
Responsable scientifique de la publicité : Monique SCHULER

---

## COMITÉ DE DIRECTION

Président : Georges MILLOT, de l'Académie des Sciences  
Pierre CHEVALLIER                      Jacques LUCAS  
Jean DERCOURT                         Daniel NAHON  
Bertrand FRITZ                         Michel STEINBERG  
Hubert de La ROCHE                   Francis WEBER

---

Echanges : Bibliothèque de l'Institut de Géologie, Betty KIEFFER, Bibliothécaire  
Ventes et abonnements : Marguerite WOLF, Régisseur

---

Editeur : Institut de Géologie, Université Louis Pasteur de Strasbourg  
et Centre de Géochimie de la Surface, CNRS  
1, rue Blessig, F-67084 STRASBOURG Cedex (France)

**Proceedings of the  
9<sup>th</sup> International Clay Conference  
1989**

Strasbourg, France, August 28 to September 2, 1989

ORGANIZED BY

Groupe français des Argiles (GFA)  
Université Louis Pasteur (ULP)  
Centre National de la Recherche Scientifique (CNRS)  
Institut Français de Recherche Scientifique pour le Développement en Coopération (ORSTOM)  
Institut National de la Recherche Agronomique (INRA)

UNDER THE AUSPICES OF

Association Internationale pour l'Etude des Argiles (AIPEA)

Volume I

**CLAY-ORGANIC INTERACTIONS  
CLAY MINERALS IN SOILS**

Editors in chief

**V.C. FARMER and Y. TARDY**

Associate Editors : R.A. EGGLETON, B. FRITZ, R. GIESE, K. KODAMA,  
H. PAQUET, J.A. RAUSSEL-COLOM and R.J. WILSON

Editing coordination : J. DUPLAY