

Geochemical markers of palaeo-environments: relations between climatic changes, vegetation and geochemistry of lake sediments, southern Brazil

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Abstract—The reconstitution of continental palaeo-environments during the recent past is generally based on the study of bio-markers such as pollen, ostracods and diatoms or on isotope markers (^{13}C , ^{18}O , ^2H). The use of these markers, however, is not always possible because of various practical limitations, e.g. time for acquisition, cost or absence in the collected material. On the other hand, one can assume that climatic changes have induced variations in the mobilization of chemical elements because weathering intensity, complexation by and nature of organic ligands, and the kinetics of erosion are greatly dependent, directly or indirectly through induced vegetation, on climatic factors.

Results of this study are based on data from a 6-m deep drill hole, near the Salitre lateritic Ti-REE deposit, southern Brazil. Pollen analysis of the sediments showed eight palaeoclimatic zones based on the changes in percentages of tree pollen during the last 30 ka. Regression and development of the forest traces a succession of humid and drier conditions through variation of the length of the dry season. Further, the nature of the forest indicated variations of the mean annual winter temperature, revealing especially, a cold and humid climate between ± 9500 and 8000 a B.P.

Chemical analysis of the sediments was performed for major and trace elements, including rare-earth elements (REE). During the most recent forest period (9500–5500 a B.P.), the La/Yb ratio, expressing REE fractionation, exhibited a drastic decrease. This can be explained by a greater complexation of heavy REE relative to the light ones, or by more acid conditions. This is entirely compatible with the particular coniferous forest (*Araucaria* forest) found at this time.

The results showed excellent correlation between the non-detrital SiO_2 content and the percentage of arboreal pollen, which increases as forest becomes dominant. This can be interpreted as the result of maximum leaching and transport of SiO_2 under a rainy climate and subsequent accumulation in the sedimentation basin.

The La/Eu ratio appears well correlated with the percentage of arboreal pollen, at least since $\pm 11,000$ a B.P.; it increases as the forest expands and diminishes during forest regression phases. Although a clear mechanism explaining this observation cannot be proposed for the moment, one can conceive that it could be related to variations of redox conditions.

All these observations are positive arguments for the use of geochemical markers as an aid for the reconstruction of climatic change

INTRODUCTION

THE RECONSTITUTION of continental palaeo-environments during the recent past is generally based on the study of bio-markers such as pollen, ostracods and diatoms, or on isotope markers (^{13}C , ^{18}O , ^2H). These markers allow an evaluation of changes of vegetation, modifications of salinity in aquatic environments and, in some cases, variations of palaeo-temperature and palaeo-precipitation. Using these markers, recent studies established the evolution of vegetation during the last 30 ka in some tropical areas of South America and Africa, and outlined the main modification of continental water balance through the oscillations of lacustrine levels (ORSTOM, 1987; USP, 1991).

It can be assumed that these climatic variations

also controlled the leaching of chemical elements. Such controls were shown on a global scale by TARDY (1969), GIBBS (1970) and GAC (1979) who demonstrated that climatic conditions (e.g. rainfall, evapotranspiration, temperature, length of dry season) are dominant factors controlling the leaching of numerous elements (Si, Al, Na, K, Ca, Mg, etc.) from soil cover toward the catchment area. On a minor scale, the nature of the vegetation induced locally by climatic conditions controls, through evapotranspiration, part of the soil water balance and thus intervenes also in leaching, i.e. in surficial transport by suspension (erosion). Furthermore, the organic matter supplied to the soils by the vegetation may also play a role in leaching through the complexing of cations, especially those having a high ionic potential like Fe, Al, Ti and REE, which are generally precipi-

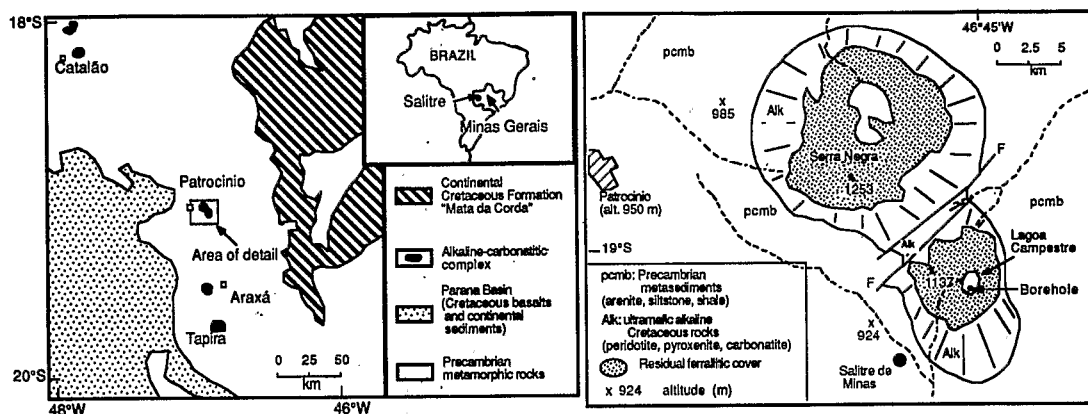


FIG. 1. Geomorphology and geology of the Salitre area, Brazil.

tated as oxy-hydroxides (ROBINSON *et al.*, 1958; FLAIG *et al.*, 1975; DUMON, 1976; REUTER and PERDUE, 1977; SCHNITZER, 1984; SHOTYK, 1984; ROBERT *et al.*, 1987; TRICHET *et al.*, 1987; PICKERING, 1989). Chelating organic acids, simple (oxalic acid, citric acid, etc.) or polymerised (fulvic acids), are produced during organic matter degradation in the soils and their production depends on the type of vegetal landscape (e.g. savanna, open forest, dense forest, etc.) and of vegetal association (broad-leaved or coniferous trees) (MARTIN, 1973; FLAIG *et al.*, 1975; KONONOVA, 1975; SCHNITZER and KAHN, 1978; BERTHELIN *et al.*, 1979; DABIN, 1980; SCHNITZER, 1984). In this regard, the REE are of particular interest because they have a high sensitivity to complexing, progressively increasing from La to Lu (HUMPHRIS, 1984; BROOKINS, 1989; WOOD, 1990a,b). Moreover, the mobility of some of them (Ce, Eu) may be affected by changes of redox conditions related to modifications of the soil moisture regime (STEINBERG and COURTOIS, 1976; BONNOT-COURTOIS, 1981; MICHEL, 1984; BROOKINS, 1988, 1989; FORTIN, 1989).

Thus, variations in the chemical exportation of elements toward the drainage systems have probably accompanied Quaternary climatic changes and the related vegetation modifications. For this reason, one can assume that geochemical signals linked to these variations could be found in contemporaneous sediments. The aim of this work was to seek and identify such signals in an appropriate site.

SITUATION OF THE SALITRE AREA

Several ultramafic-alkaline complexes occur in the west of Minas Gerais State (Brazil) and in the Alto Paranaíba area (ULBRICH and GOMEZ, 1981). One of these, the Salitre complex, composed mainly of carbonatites and micaceous pyroxenites, has a central, dolina-shaped, depression ("Lagoa Campestre") partially filled by sediments and occupied by a lake (Fig. 1). A thick, loose latosolic cover (hematite, goethite, gibbsite, kaolinite, quartz, anatase, crandallite family phosphates) surrounds the depression, overlying a thick saprolite (50–100 m). Due to the particular mineralogy of the bedrock, where perovskite, calzirtite and apatite are often essential minerals, these alterites have high

contents in TiO_2 (up to 30%), REE (5% $\Sigma \text{RE}_2\text{O}_3$), ZrO_2 (1%) and Nb_2O_5 (1%).

The climate is tropical, characterized by a mean annual temperature of $\pm 21^\circ\text{C}$ and a rainfall of ± 1400 mm; the length of the dry season reaches four months. The original vegetation, nowadays largely modified by human activity (coffee and ranch), consists of arboreal savanna ("cerrado") and patches of moist semideciduous forest.

SEDIMENTARY SEQUENCE AND RADIOCARBON AGES

Lake sediments were sampled in the Lagoa Campestre using a 3" (7.6 cm) vibro-corer at a distance of ~100 m from the margin (Fig. 1). The hole reached bedrock at 6 m and crossed (i) in the upper part, down to 3 m, a blackish to brownish organo-mineral deposit rich in plant fibres (organic C content from 40 to 50%); (ii) in the lower part, brownish concretionary clayey layers poorer in organic C (10–15%).

Radiocarbon ages were measured at some levels in the upper horizon (Fig. 2). The dates indicate continuous sedimentation from $\pm 17,000$ a B.P. (164 cm) until ± 3000 a B.P. (18 cm). Below this level, there is a hiatus until an age of nearly 29,000 a B.P. was found at 170 cm. The detailed work presented hereafter only concerns the upper, well-dated part of the core.

PALYNOLOGY

The results of the palynological study (LEDRU, 1991a,b,c), carried out following classical methods, are shown in Fig. 2. The results are expressed in percentages of each taxon, with the percentages calculated with respect to the sum of the arboreal pollen (AP), the non-arboreal pollen (NAP) and the undetermined pollen. Aquatic and hygrophilic taxa are excluded from this sum, as are spores. The palynological spectra were compared with those obtained at the present time in various vegetal associations of southern Brazil whose distribution is mainly controlled by climatic parameters (temperature, length of dry season, ...). A rough evaluation of the palaeoclimatic conditions was thus possible.

Eight palaeoclimatic zones were recognized during the last 30 ka. Regression and development of the forest point out a succession of humid and drier conditions through the variation of the length of the dry season. Furthermore, the nature of the forest indicates variations of the mean annual

winter temperature, revealing especially a cold and humid climate between ±9500 and 8000 a B.P.

GEOCHEMISTRY

The geochemical sampling was performed within a 2-cm interval above or below the palynological sampling and multielement chemical analysis made.

After drying at 60°C, the samples were crushed and sieved (200 μm). The loss on ignition (LOI) was determined by weighing after heating to 1000°C. The chemical composition was determined after melting with LiBO₂ and dilution in 2N HNO₃. The content of SiO₂, Al₂O₃, Fe₂O₃, TiO₂, MnO, P₂O₅, REE and other trace elements were analysed using ICP-AES, while Na₂O, K₂O, MgO and CaO were analysed using AAS. Carbon and N were determined with a CHN elemental analyser.

In conjunction with the chemical analysis, grain-size analysis and mineralogical investigations (optical, XRD and electron microprobe) were carried out.

In Fig. 3, showing the chemical composition of the sediments, the high LOI indicates a high organic matter content throughout the record as confirmed by a C content ranging from 40 to 50%. On the other hand, Si and Al are the main components of the mineral fraction which consists of a mixture of quartz, opal, gibbsite, kaolinite, anatase, phosphates of the crandallite group, and scarce heavy minerals (ilmenite, calzirtite, zircon, baddeleyite, barite).

Table 1 presents the contents of REE and Y contents, which are very high and increase with depth, light REE always predominating over the heavy REE. The high contents and the predominance of LREE evidently reflect an inheritance from the carbonatitic parent material. No significant correlation was found between the REE and the major elements.

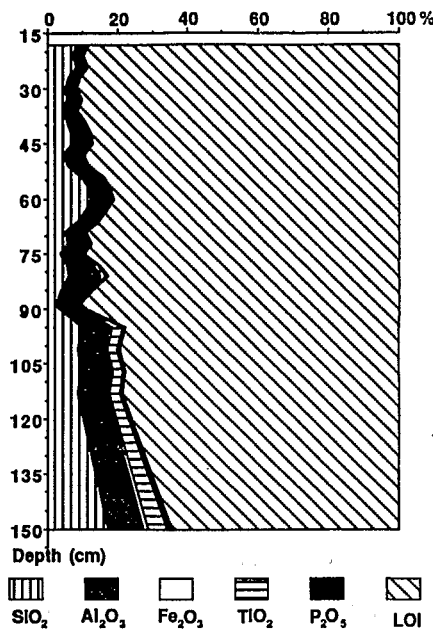


Fig. 3. Chemical composition of the sediments (LOI = loss on ignition).

GEOCHEMICAL MARKERS

Three chemical parameters (La/Yb, SiO₂ and La/Eu) were of particular interest as geochemical indicators of vegetation modifications and climatic changes.

During the most recent forest period (9500–5500 a B.P.), the La/Yb ratio, expressing REE fractionation, shows a drastic decrease (Fig. 4). Because REE are easily complexed, more so for HREE than for LREE, either by inorganic ligands (HUMPHRIS, 1984; BROOKINS, 1989; WOOD, 1990a,b) or by organic ligands (TURNER *et al.*, 1981; BRUQUE *et al.*, 1982; CANTRELL and BYRNE, 1987), this variation might be the result of a greater production of chelating agents in soils during this period. This is in good agreement with the particular coniferous forest (*Araucaria* forest) which only developed at this time and was not present during the older forest episode. Indeed, it is well established that, under coniferous cover, the degradation of soil organic matter produces greater amounts of fulvic acid, which has a high chelating capacity (KONONOVA, 1975; SCHNITZER and KAHN, 1978; DUCHAUFOR, 1979).

As shown in Fig. 5, there is an excellent correlation between the SiO₂ content and the percentage of arboreal pollen: SiO₂ increases as the forest dominates. Because no correlation was found between SiO₂ and Al₂O₃, this increase is not related to the inflow of kaolinite. The grain-size analysis indicated that the ≥20 μm fraction of the sediment, containing the detrital quartz, was always low (<5%); on the other hand, mineralogical analysis revealed abundant amorphous SiO₂ (opal) in the silt fraction. One

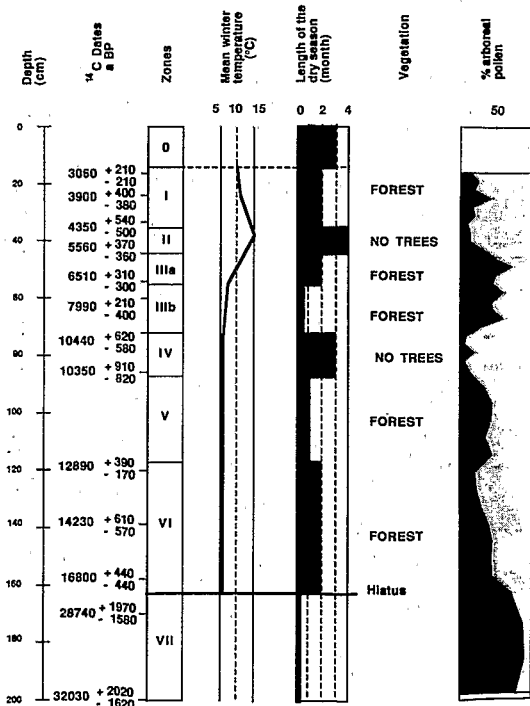


Fig. 2. Age, palynology and palaeoclimatic reconstruction.

Table 1. REE and Y contents in studied core; all values in ppm

Depth (cm)	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu	ΣREE	Y
17-18	17.6	35.0	12.5	2.2	0.5	1.4	0.9	0.6	0.31	0.04	75.5	4.5
20-21	18.7	37.6	12.4	2.3	0.5	1.6	0.9	0.7	0.32	0.06	79.6	4.6
23-24	20.4	28.0	13.0	2.1	0.5	1.6	0.9	0.6	0.32	0.07	82.6	4.9
26-27	16.4	29.8	10.6	1.7	0.4	1.4	0.7	0.5	0.25	0.06	65.8	3.9
29-30	16.2	30.6	11.0	2.0	0.5	1.6	0.9	0.6	0.29	0.05	67.7	4.0
32-33	21.7	38.5	14.3	2.3	0.6	1.5	1.1	0.8	0.40	<0.02	86.9	5.7
35-36	18.5	35.0	12.9	2.1	0.5	1.6	0.9	0.9	0.30	<0.02	77.6	5.0
38-39	31.6	56.8	20.0	3.6	0.8	2.6	1.6	1.0	0.45	0.08	125.5	7.1
41-42	40.3	69.0	24.7	4.3	1.0	3.0	1.9	1.0	0.52	0.07	154.4	8.6
44-45	52.1	86.2	30.4	5.2	1.2	3.9	2.3	1.2	0.63	0.11	193.4	10.0
47-48	36.2	62.4	20.6	3.4	0.8	2.5	1.6	0.9	0.40	0.10	135.9	7.1
50-51	68.4	114.5	37.9	6.3	1.5	4.3	2.6	1.5	0.70	0.10	251.2	13.4
53-54	79.0	129.6	45.3	7.5	1.9	5.7	3.3	1.6	0.85	0.16	289.5	14.6
56-57	87.8	145.5	51.2	8.5	2.0	6.2	3.6	1.7	0.92	0.17	323.9	16.4
59-60	89.2	153.4	53.1	8.5	2.0	6.0	3.4	1.6	0.88	0.14	334.6	16.4
62-63	69.9	124.4	43.0	7.1	1.7	5.2	2.8	1.4	0.72	0.12	269.1	12.8
65-66	86.2	148.9	52.8	8.3	2.0	5.6	3.2	1.7	0.80	0.10	326.2	16.7
68-69	94.5	163.6	62.0	9.7	2.4	7.7	3.6	1.9	0.80	0.10	362.7	16.4
71-72	116.7	196.3	77.7	12.5	3.1	8.4	4.4	1.9	1.04	0.18	439.3	17.2
74-75	109.7	191.7	74.2	11.9	2.8	7.6	4.1	2.0	1.00	0.10	423.0	17.9
77-78	176.0	307.4	119.2	18.6	4.7	12.3	6.4	2.9	1.50	0.20	675.3	26.4
80-81	195.9	353.2	138.7	21.9	5.3	15.3	7.6	3.1	1.75	0.29	770.7	27.8
83-85	145.3	253.2	98.5	15.6	3.9	10.3	5.5	2.5	1.20	0.20	559.0	22.8
87-89	84.1	156.7	59.8	9.7	2.4	6.5	3.2	1.5	0.75	0.14	336.6	11.9
93-95	271.4	469.3	192.7	31.1	7.7	19.7	10.4	4.1	2.33	0.41	1046.3	37.2
99-101	250.5	445.6	182.1	29.2	7.2	18.6	9.8	3.8	2.20	0.36	984.4	35.1
105-107	316.4	600.9	247.6	38.2	9.3	24.0	12.7	5.0	2.70	0.30	1304.6	47.6
111-113	274.2	482.8	195.5	31.9	7.8	19.7	10.8	4.2	2.33	0.40	1067.5	38.1
147-150	479.4	920.9	372.3	60.4	14.8	39.0	19.7	7.8	4.39	0.75	1989.9	70.4

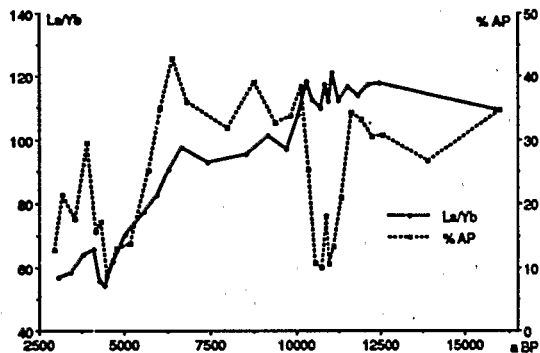


FIG. 4. Variation of the La/Yb ratio with respect to arboreal pollen (AP) percentages.

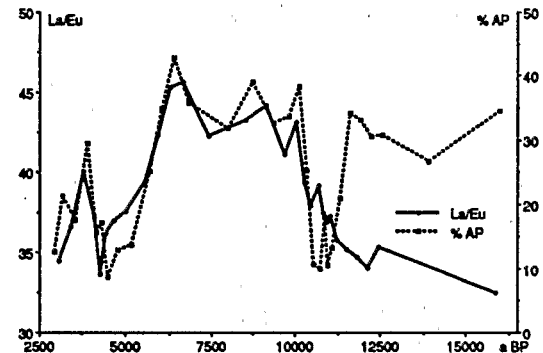
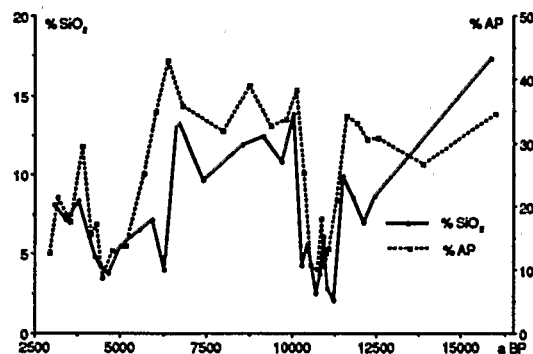


FIG. 6. Variation of the La/Eu ratio with respect to arboreal pollen (AP) percentages.

FIG. 5. Variation of the SiO₂ content with respect to arboreal pollen (AP) percentages.

can thus assume that the SiO₂ peaks concordant with forest development are mainly related to soluble inputs rather than to clastic ones. This is in agreement with both the lowering of the erosion rate under forest cover and with a probable greater soluble SiO₂ exportation induced by the weathering conditions prevailing in such an environment. Indeed, high SiO₂ levels are generally found in ground waters under tropical rainforest (GRIMALDI, 1988); they could be related to the higher fulvic acid content of tropical forest soils (MARTIN, 1973; DABIN, 1980) whose hydrolytic action with silicates is well known (ROBERT *et al.*, 1987).

After ±11,000 a B.P., the La/Eu ratio (Fig. 6) is well correlated with the percentage of arboreal pol-

len; it increases as the forest expands and decreases during forest regression phases. A similar correlation is obtained for the Ce/Eu ratio but not for the ratio of other analysed REE. A clear explanation for this pattern of variation cannot be advanced at the moment, but it could be related to changes in the redox conditions. According to BROOKINS (1988), Eu is the only REE which can exist under the reduced state (Eu^{2+}), but only at very low Eh. Another possibility might be a metabolic fractionation for Ce, as reported by ROBINSON *et al.* (1958).

CONCLUSIONS

The comparison of geochemical and mineralogical data with the palynological record in the sediments of a lake in southern Brazil allowed the recognition of three geochemical signals (La/Yb, SiO_2 , La/Eu) possibly related to changes of vegetation and climate.

The REE fractionation, expressed by the La/Yb ratio, seems to be influenced by the amount and quality of complexing products present in the weathering zone. In the Salitre area, the level of the REE is high, due to the particular mineralogy of the bedrock. However, the mechanisms involved in the REE fractionation are probably of general significance and this parameter should thus be tested elsewhere.

Despite the ubiquity of H_4SiO_4 in soil solutions, its easy reaction with Al will lead to the immobilization of SiO_2 in most cases. In the present study, it is likely that the SiO_2 signal is usable because, in the neighbouring latosilic cover, Al_2O_3 is essentially trapped in Al-goethite or in gibbsitic ferruginous microaggregates and is thus poorly reactive.

No simple explanation for the behaviour of the La/Eu ratio is available at the moment.

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REFERENCES

- BERTHELIN J., SOUCHIER B. and TOUTAIN F. (1979) Intervention des phénomènes biologiques dans l'altération. *Science Sol* 2-3, 175-187.
- BONNOT-COURTOIS C. (1981) Géochimie des Terres Rares dans les principaux milieux de formation et de sédimentation des argiles. Thesis University Paris XI, Orsay.
- BROOKINS D. G. (1988) *Eh-pH Diagrams for Geochemistry*. Springer.
- BROOKINS D. G. (1989) Aqueous geochemistry of REE. In *Geochemistry and Mineralogy of REE* (eds B. R. LIPIN and G. A. MCKAY), Reviews in Mineralogy, Vol. 21, pp. 201-225. Mineral. Soc. Am.
- BRUQUE S., MORENO-REAL L., MOZAS T. and RODRIGUEZ-GARCIA A. (1982) Interlayer complexes of Lanthanide montmorillonites with amines. *Clay Minerals* 17, 201-208.
- CANTRELL K. L. and BYRNE R. H. (1987) REE complexation by carbonate and oxalate ions. *Geochim. cosmochim. Acta* 51, 597-605.
- DABIN B. (1980) Les matières organiques dans les sols tropicaux normalement drainés. Cah. ORSTOM, sér. Pédol. 18, 197-215.
- DUCHAUFOUR P. (1979). *Pédologie, Vol. 2: Constituants et Propriétés des Sols*. Masson.
- DUMON J. C. (1976) Action d'acides organiques divers sur les minéraux titanés (ilménite et rutile). Comparaison de leur pouvoir d'extraction du titane avec celui d'acides minéraux. *Bull. Soc. Géol. France* 28, 75-79.
- FLAIG W., BEUTELSPACHER H. and RIETZ E. (1975) Chemical composition and physical properties of humic substances. In *Soil Components, Vol. 1: Organic Components* (ed. J. E. GIESEKING), pp. 1-211. Springer.
- FORTIN P. (1989) Mobilisation, fractionnement et accumulation des Terres Rares lors de l'altération latéritique de sédiments argilo-sableux du bassin de Curitiba (Brésil). Mém. Sci. Terre, Ecole des Mines de Paris, 10.
- GAC J. Y. (1979) Géochimie du bassin du lac Tchad. Bilan de l'altération, de l'érosion et de la sédimentation. Thèse University. L. Pasteur, Strasbourg.
- GIBBS R. J. (1970) Mechanisms controlling world water chemistry. *Science* 170, 1088-1090.
- GRIMALDI C. (1988) Origine de la composition chimique des eaux superficielles en milieu tropical humide: exemple de deux petits bassins versants sous forêt en Guyane française. *Sci. Géol. Bull.* 41, 247-262.
- HUMPHRIS S. E. (1984) The mobility of the REE in the crust. In *Rare Earth Element Geochemistry* (ed. P. HENDERSON), pp. 317-342. Elsevier.
- KONONOVA M. M. (1975) Humus of virgin and cultivated soils. In *Soil Components, Vol. 1: Organic Components* (ed. J. E. GIESEKING), pp. 475-526. Springer.
- LEDRU M. P. (1991a) Etude de la pluie pollinique actuelle des forêts du Brésil central: climat, végétation, application à l'étude de l'évolution paléoclimatique des 30 000 dernières années. Thesis, Museum National Histoire Naturelle, Paris.
- LEDRU M. P. (1991b) Modifications de la végétation du Brésil Central entre la dernière époque glaciaire et l'interglaciaire actuel. *C. R. Acad. Sci. Paris, Sér. II* (in press).
- LEDRU M. P. (1991c) Late Quaternary environmental and climatic changes in Central Brazil, Salitre, 19°S. *Quat. Res.* (in press).
- MARTIN D. (1973) Les horizons supérieurs des sols ferrallitiques sous forêt et sous savanne du Centre-Cameroun. Cah. ORSTOM, Sér. Pédol. 11, 155-179.
- MICHEL J. J. (1984) Occurrence du Cerium dans les épisynites uranifères du Bernardan (Haute Vienne, France): témoins d'altérations continentales oxydantes. *C. R. Acad. Sci. Paris, Sér. II* 299, 245-248.
- ORSTOM (1987) Paéolacs et paléoclimats en Amérique latine et en Afrique (20.000 ans B.P.-actuel). *Géodynamique* 2, 91-174.
- PICKERING W. F. (1989) The competing role of dissolution, sorption and complex formation in element mobilisation. In *Weathering; its Products and Deposits*, Vol. 1, pp. 259-305, Processes. Theophrastus.

- REUTER J. H. and PERDUE E. M. (1977) Importance of heavy metal-organic matter interactions in natural waters. *Geochim. cosmochim. Acta* **41**, 325-334.
- ROBERT M., RAZZAGHE M. H. and RANGER J. (1987) Rôle du facteur biochimique dans la podzolisation. In *Polzols et Podzolisation*, INRA-AFES, Paris, pp. 207-223.
- ROBINSON W. O., BASTRON H. and MURATA K. J. (1958) Biogeochemistry of the rare-earth elements with particular reference to hickory trees. *Geochim. cosmochim. Acta* **14**, 55-67.
- SCHNITZER M. (1984) Soil organic matter: its role in the environment. In *MAC Short Course Handbook, Vol 10: Environmental Geochemistry*, pp. 237-267.
- SCHNITZER M. and KAHN S. U. (1978) *Soil Organic Matter*. Elsevier.
- SHOTYK W. (1984) Metal-organic species in natural waters. In *MAC Short Course Handbook, Vol 10: Environmental Geochemistry*, pp. 45-65.
- STEINBERG M. and COURTOIS C. (1976) Le comportement des Terres Rares au cours de l'altération et ses conséquences. *Bull. Soc. Géol. France* **18**, 13-20.
- TARDY Y. (1969) Géochimie des altérations. Etude des arènes et des eaux de quelques massifs cristallins d'Europe et d'Afrique. *Mém. Serv. Carte Géol. Als. Lorr.* 31.
- TRICHET J., DISNAR J. R., BONNAMY S., GAUTHIER B., NAKASHIMA S., OBERLIN A., PERRUCHO A. and ROUZAUD J. N. (1987) Le comportement mutuel de la matière organique et des métaux: implications géochimiques et métallogéniques. *Mém. Soc. Géol. France*, **151**, Géologie de la Matière Organique, 143-162.
- TURNER D. R., WHITFIELD M. and DICKSON A. G., (1981) The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm pressure. *Geochim. cosmochim. Acta* **45**, 855-881.
- ULBRICH H. H. and GOMEZ C. B. (1981) Alkaline rocks from continental Brazil. *Earth Sci. Rev.* **17**, 135-154.
- USP (1991) International Symposium on Global Changes in South America during the Quaternary. São Paulo, Brazil, May 8-12, 1989, Bol. IG-USP **8**.
- WOOD A. S. (1990a) The aqueous geochemistry of the REE and Y. 1—Review of available low-temperature data for inorganic complexes and the inorganic REE speciation of natural waters. *Chem. Geol.* **82**, 159-186.
- WOOD A. S. (1990b) The aqueous geochemistry of the REE and Y. 2—Theoretical predictions of speciation in hydrothermal solutions to 350°C at saturation water vapor pressure. *Chem. Geol.* **88**, 99-125.