

Mg-Mica Formation in Alkaline Environment of the Nhecolândia, South Mato Grosso, Brazil

S.C.Furquim, J.P.Queiroz Neto, S.Furian

Department of Geography, University of São Paulo, São Paulo, Brazil

L.Barbiéro

Department of Metallurgy, Indian Institute of Science, Bangalore, India

R.C.Graham

Department of Environmental Sciences, University of California, Riverside, USA

ABSTRACT: The geochemical control of Mg in alkaline environment is still subject to debate. Precipitations of stevensite, sepiolite or Mg-montmorillonite are usual in alkaline water but the formation of Mg-silicate has been more deduced from geochemical equilibrium between solid and liquid phase than actually observed from mineralogical investigations. The knowledge of exact stoichiometry involved in Mg precipitation is necessary to elaborate a chemical tracer in order to realize hydro-chemical balances. In the Nhecolândia, a sub-region of the Pantanal wetland in Brazil, recent studies have shown that saline water arises from present day concentration of fresh water under the influence of evaporation. The geochemical processes involving the major elements as the solutions become more saline are the precipitation of calcite or Mg-calcite, magnesium-silicates and eventually sodium-carbonates. In the Pantanal framework, the precipitations occur in sandy horizons, making possible the accurate identification of the Mg-involving silicate formation. The clay (<2 μ m) and medium silt fractions were analysed using x-ray diffraction, microprobe SX50, and observed under SEM and TEM. The results indicate that magnesium is incorporated in small quantities (2 to 3 %) in amorphous material and in the neof ormation of a low-charge mica. The consequences in term of hydro-chemical budget are presented.

1 INTRODUCTION

The geochemical control of Mg²⁺ in natural alkaline waters subjected to evaporation has been reported in the literature through two main processes: 1) precipitation of Mg-carbonates (Cheverry 1974, Eugster & Hardie 1978, Barbiéro 1995) and 2) formation of Mg-silicates (Garrels & Mackenzie 1967; Gac et al. 1977, Jones et al. 1977, Jones & Galan 1988, Valles et al 1989; Marlet et al. 1996).

The first process seems to occur when the Mg/Ca ratio of diluted waters increases after calcite precipitation, being responsible for the origin of endogenic minerals as Mg-calcite and magnesite (Eugster & Hardie, 1978). The second process apparently takes place in the early stages of water concentration (Gac et al. 1977) and possibly occurs both in waters depleted and enriched in Al, producing stevensite and sepiolite in the former (Darragi & Tardy, 1987) and smectite in the latter (Jones 1986; Valles et al. 1989). Stevensite (Velde 1985, Jones 1986, Torres Ruiz et al. 1994) and sepiolite (Garrels & Mackenzie 1967, Gac et al. 1977, Torres Ruiz et al 1994, Singer et al. 1998) are usually considered as endogenic minerals when formed in highly evaporative environments. Smectite, however, seems to be formed either by

direct precipitation (endogenic origin) or by transformation from pre-existing clays (authigenic origin) (Gac et al. 1977). However, the formation of these minerals has been more frequently predicted through geochemical equilibrium between solid and liquid phase than actually observed from mineralogical investigations (Gac et al. 1977, Valles et al. 1989, Marlet et al. 1996). In most of the studies, the exact stoichiometry involved in the Mg control processes has not been accurately identified.

The identification of the processes involved in the water evolution of alkaline environments, including those related to the Mg control, can provide important information in order to elaborate a quantitative tracer for the hydro-bio-geochemical balance (Ribolzi et al. 1996; Barbiéro et al. 2001).

The Nhecolandia, a sub-region located in the Pantanal wetland in central-western Brazil (16°-20°S and 50°-58°W), presents as a distinctive feature both freshwater and saline lakes with a huge chemical variability, and co-existing in close proximity, the latter currently evolving in an alkaline way under the influence of concentration by evaporation (Valles et al. 1991). The processes responsible for most water chemical variability are the precipitation of calcite or Mg calcite, the formation of Mg silicates and

eventually Na-carbonates as water becomes more saline (Barbiéro et al. 2002). In this sub-region of Pantanal wetland, most of the sediments and soil materials are sandy (Del'Arco et al. 1982; Silva 1986; Queiroz Neto et al. 1997), which favors the discrimination of the neoformed minerals from pre-existing clays and allows the accurate identification of the Mg-silicate stoichiometry.

The objective of this study is to identify mineralogical composition of Mg-clay suspected to be responsible for the control of Mg in the soil solution.

2 MATERIALS AND METHODS

The present study was achieved at Nhumirim Farm (18°59'S and 56°49'W) and sampling was around a representative saline lake of Nhecolândia, that is, with pH values ranging from 5.5 to 11.5 and EC ranging from 50 microS cm⁻¹ to 60 milliS cm⁻¹. The soil materials around this lake are formed by a light, sandy and structureless surficial horizon, which overlies a light and sandy horizon with abundant blackish volumes of organic matter, polyedric substructure and with common presence of carbonate nodules. Beneath, there is a green horizon (5Y 5/2), containing higher amount of clay (12 to 20%), structureless sodic and alkaline (Na/T>50 % and pH ranging from 9 to 11) (Barbiero et al. 2000).

X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses were performed on the gray and green horizons whereas transmission electron microscopy (TEM) analysis was performed only in the latter.

X-ray diffraction analyses were accomplished on silt and clay fractions, both of them separated by centrifugation and sedimentation after destruction of the organic matter with NaOCl (pH 9.5) (Anderson, 1963). Oriented specimens were analyzed through five different treatments: ethylene glycol solvation, Mg saturation, K saturation and heating of the K saturated clay at 350°C and 550°C (Jackson 1979) using a Siemens D-500 diffractometer (CuK radiation with graphite crystal monochromator). Analyses were run with a step size of a 0.02° 2θ and a count time of 1.0 s per step.

Samples of the whole soil material and the medium silt fraction were examined using a FEI XL30-FEG SEM fitted with a semi-quantitative elemental analyser (EDAX).

The <2µm clay fraction of the green layer was selected for analysis using a FEI-CM300 TEM linked with a x-ray detector EDS, model Phoenix, and with a elemental analyzer EDAX. A drop of a diluted suspension with the clay was placed on a standard Cu grid with carbon film.

Quantitative analyses were performed on compacted clay patches using electronic microprobe SX50 fitted with wavelength dispersive spectrometers (WDS).

3 RESULTS AND DISCUSSION

The microprobe analysis indicates that the clay fraction of both grey and green horizons is composed of Si (60 to 70%), and secondary of Al (15 to 25%), K (6 to 9%), Fe (4 to 7%), Mg (2 to 3%) and Ca (1 to 6 %). The mineralogical composition of the clay fraction consists mainly of mica, kaolinite and quartz (Figure 1). The medium silt is dominated by quartz in the gray horizon whereas it presents a mineral composition similar to that of the clay fraction in the green layer. The SEM observations revealed that this medium silt fraction in the green horizon is composed of clay aggregates rather than silt-sized mineral grains.

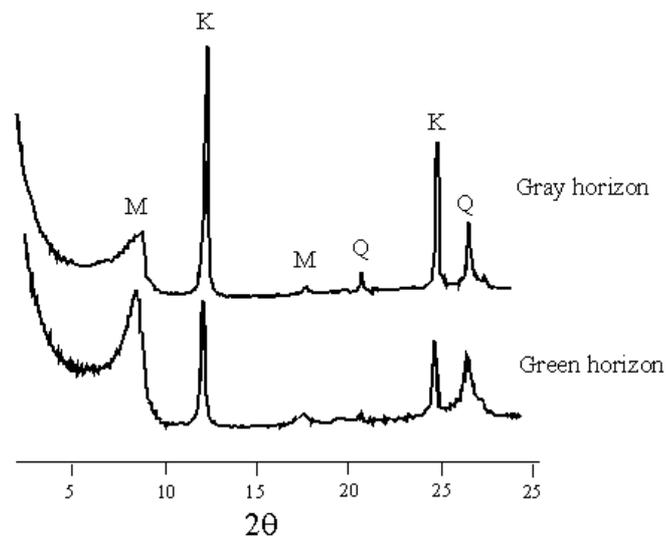


Figure 1: X-ray patterns of clay in both gray and green horizons. M: mica; K: kaolinite; Q: quartz.

The TEM analysis was consistent with both x-ray diffraction and SEM results, as mainly amorphous materials enriched in Si and a well-crystallized low charge mica were identified (Figure 2). According to this preliminary observation, it seems that the clay mineralogy of the <2µm fraction and medium silt fraction may be arising from precipitation of mica in a matrix of amorphous silica-rich phase. Grey and green horizon, that were clearly distinguished in the field, differ mainly in the composition of the silt fraction, which is predominantly composed of quartz in the first one and of quartz grains and clay aggregates in the second one. Neoformation of mica from smectite has already been described in African alkaline lakes (Singer & Stoffers 1980; Jones &

Weir 1983). To our knowledge, direct neoformation of mica or crystallization of mica from amorphous material has never been described in alkaline environments.

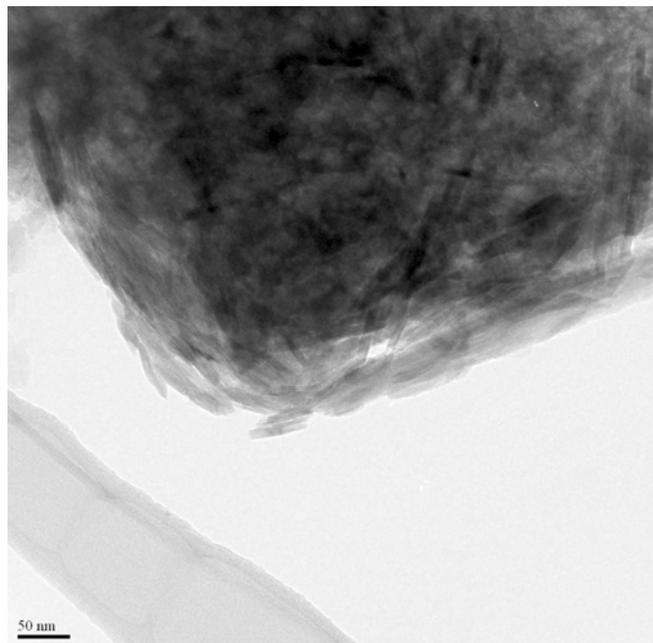


Figure 2. Amorphous silica-rich phase with mineral crystallization, identified in the TEM.

The results also indicate that Mg is not a major component of the neoformed clay fraction, which presents higher K contents. The results are in agreement with the geochemical studies carried out at the regional scale (Barbiéro et al. 2000) that emphasized that Mg was controlled by both carbonate and silicate precipitation.

The formation of Mg-involving silicates may have a significant influence in the control of Mg, because Mg is present in low quantities in the water. Even though the proportion of K is higher in the precipitating clay, the clay formation may have much less effect on K contents in the solution because they are about 100 times higher than Mg contents in the equilibrating solution (Barbiéro et al. 2002).

4 CONCLUSIONS

The first investigations carried out on the clay and silt fraction seems to indicate that the green horizon developed around and beneath the saline lakes of the Nhecolândia is composed of amorphous silica in which the neoformation of a mica is occurring. These formations involve transfer of protons that should be taken into account in the hydro-geochemical balance carried out on these alkaline lakes.

Although the proportion of Mg involved is low, clay precipitation may contribute significantly in the control of magnesium in the soil solution, and may have a strong qualitative impact on the water chemistry. The next research efforts should focus first on the proportion of Mg included in the Mg-calcite, and then on the simulation of evaporation taking into account Mg-calcite precipitation and the clay neoformation identified in this study.

5 REFERENCES

- Anderson, J.U., 1963. An improved pretreatment for mineralogical analysis of samples containing organic matter. *Clays Clay Miner.* 10:380-388.
- Barbiéro, L., 1995. Les sols alcalinisés sur socle dans la vallée du fleuve Niger. Origine de l'alcalinisation et évolution des sols sous irrigation. *Travaux et Documents Microfichés Orstom* 138, 209 p.
- Barbiéro, L., Valles, V., Regard, A., Cheverry, C., 2001. Residual alkalinity as tracer to estimate the changes induced by a forage cultivation in a non-saline irrigated sodic soil. *Agricultural Water Management* 50: 229-241.
- Barbiéro, L., Queiroz Neto, J.P., Ciornei, G., Sakamoto, A.Y., Capellari, B., Fernandes, E., Valles, V., 2002. Geochemistry of water and ground water in the Nhecolândia, Pantanal of Mato Grosso, Brazil: variability and Associated processes. *Wetlands* 22: 528-540.
- Barbiéro, L., Queiroz Neto, J.P., Sakamoto, A. 2000. Características geoquímicas dos solos relacionados à organização pedológica e à circulação de água (Faz. Nhumirim da EMBRAPA, Nhecolândia, MS). III Simpósio sobre Recursos Naturais e Sócio-Econômicos do Pantanal. Corumbá, 27 a 30 de novembro de 2000.
- Cheverry, C., 1974. Contribution à l'étude pédologique des polders du lac Tchad. Dynamique des sels en milieu continental subaride dans les sédiments argileux et organiques. Thesis. Sci., U.L.P. Strasbourg, 257 pp.
- Darragi, F., Tardy, Y. 1987. Authigenic trioctahedral smectites controlling pH, alkalinity, silica and magnesium concentrations in alkaline lakes. *Chemical Geology*, 63: 59-72
- Del'Arco, J.O., Silva, R.H. Tarapanoff, I. Freire, F.A. Pereira, L.G. Souza, S.L. Luz, D.S. Palmeira, R.C.B. Tassinari, C.C.G., 1982. Geologia da Folha SE.21 Corumbá e Parte da Folha SE.20. In *Radam Brasil-Levantamento dos Recursos Naturais*. Rio de Janeiro, p.25 a 160.
- Eugster, H.P., Hardie, L.A., 1978. Saline Lakes. In Lerman, A. (ed.) *Lakes: chemistry, geology and physics*. Springer-Verlag, p. 237-294.
- Gac, J.Y., Droubi, A., Fritz, B., Tardy, Y., 1977. Geochemical behavior of silica and magnesium during the evaporation of waters in Chad. *Chemical Geology* 19, 215-228.
- Garrels, R.M., Mackenzie, F.T., 1967. Origin of the chemical compositions of some springs and lakes. In *Equilibrium Concepts in Natural Water Systems*. Am. Chem. Soc., Adv. Chem. 67:222-242.
- Jackson, M.L., 1979. *Soil Chemical Analysis-Advanced Course*. 2nd ed. M.L. Jackson, Madison, WI.
- Jones, B.F., Galan, E., 1988. Palygorskite-sépiolite. In *Hydrous phyllosilicates exclusive of Micas*. S.W. Bailey (Ed.), *Geol. Soc. Amer. Reviews in Mineralogy*, 19, 725 p. (631-674)

- Jones, B.F., 1986. Clay mineral diagenesis in lacustrine sediments. In: Mumpton, F.A. (Ed.), *Studies in Diagenesis*. US Geol. Surv. Bull. 1578, 291–300.
- Jones, B.F., Eugster, H.P., Rettig, S.L., 1977. Hydrochemistry of Lake Magadi Basin, Kenya. *Geochim. Cosmochim. Acta* 41, 53–72.
- Jones, B.F., Weir, A.H., 1983. Clay minerals of Lake Abert, an alkaline, saline lake. *Clays and Clay Minerals* 3:161–172.
- Marlet, S., Valles, V., Barbiero, L., 1996. Field Study and Simulation of Geochemical Mechanisms of Soil Alkalinization in the Sahelian Zone of Niger. *Arid Soil Research and Rehabilitation*, 10:243-256.
- Queiroz Neto, J.P.; Sakamoto, A.; Lucati, H.M.; Fernandes, E. (1996) Dinâmica Hídrica e de uma Lagoa Salina e seu entorno na Área do Leque, Nhecolândia, Pantanal- MS. In II Simpósio sobre Recursos Naturais e Sócio-Econômicos do Pantanal. Corumbá, MS, p.51.
- Ribolzi, O., Valles, V., Bariac, T., 1996. Comparison of hydrograph deconvolutions using residual alkalinity, chloride and oxygen 18 as hydrochemical tracers. *Water Resources Research*, 32:1051-1059
- Silva, T.C. (1986) Contribuição da Geomorfologia para o Conhecimento e Valorização do Pantanal. In Anais do 1o Simpósio sobre Recursos Naturais e Sócio-Econômicos do Pantanal, 27 de novembro a 4 de dezembro de 1984, Corumbá (MS), 77-90.
- Singer, A., Stoffers, P., 1980. Clay mineral diagenesis in two East African lakes. *Clay Minerals* 15: 291-307.
- Singer, A., Stahr, K., Zarei, M., 1998. Characteristics and origin of sepiolite (Meerschaum) from Central Somalia. *Clay Minerals* 33: 349–362.
- Torres Ruiz, J., López-Galindo, A., González-López, J.M., Delgado, A., 1994. Geochemistry of Spanish sepiolite-palygorskite deposits: genetic considerations based on trace elements and isotopes. *Chemical Geology*, 112: 221-245.
- Valles, V., N'Diaye, M.K., Bernadac, A., Tardy, Y., 1989. Geochemistry of waters in the Kouroumari Region, Mali; Al, Si, and Mg in Waters Concentrated by Evaporation: Development of a Model. *Arid Soil Research*, 3: 21-39.
- Valles, V., Pachepsky, I., Ponizovsky, A.A., 1991. Invariant criteria for irrigation water quality assessment in arid and semi-arid regions. In : *Genesis and Control of Fertility of Salt Affected Soils*. ISSS Subcommittee on Salt Affected Soils Science, pp. 330-333 USSR, V.V. Dokuchaev Soil Institute, Moscow.
- Velde, B., 1985. *Clay Minerals: a physico-chemical explanation of their occurrence*. Developments in Sedimentology, 40. Elsevier, 427 p.

6 ACKNOWLEDGEMENTS

This work was developed in the framework of a Capes-Cofecub Cooperation n°412-03.