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Correlation of the chemical composition of water from the unsaturated zone with the mineralogy of a profile on the São Paulo Basin, Brazil

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ABSTRACT: In this paper the correlation between water from the unsaturated zone and the mineralogy of the weathered sedimentary profile is treated. These studies were carried out at an Experimental Station installed on the Campus of the University of São Paulo. The lithology consists of successive layers of clays, silts, sands and clayey sands below a surface soil and the mineralogy is mainly composed of quartz, kaolinite, smectite, goethite, in lesser quantities muscovite, and rarely microcline. All are detrital and the kaolinite originated from the weathering of muscovite and microcline. The results showed that there is a kaolinitization process on the muscovite and the microcline, however small, setting free the K^+ which is reflected in higher concentration of this element in the percolating waters.

1. INTRODUCTION

With the objective to study the chemical composition of water from the unsaturated zone and the correlated phenomena, an Experimental Station was installed on the Campus of the University of São Paulo (São Paulo, Brazil).

The purpose of this paper was to establish the correlation between the chemical composition of waters and the mineralogical compositions of various levels through phase diagrams and by petrographic studies which would indicate the resulting mineralogical evolution of the geological material and the percolating waters.

The Experimental Station is situated on the sedimentary basin of São Paulo, of Tertiary age. The origin of the sediments is fluvial and consists, predominantly, of sands, siltic clays and clays.

2. METHODOLOGY

For water sampling porous cups were installed at 0.50-0.50 m intervals, beginning from the surface till a depth of more or less 10.50 m, or the groundwater level.

The water monitoring consisted of weekly samplings, during a 14 month period (October 1985-January 1987).

The following determinations were carried out "in situ": pH, Eh, water and air temperatures, electrical conductivity, dissolved O_2 and CO_2; HCO_3^- and/or CO_3^{2-} and NH_4^+. At the laboratory the concentrations of Ca^{2+}, Mg^{2+}, Al^{3+} and Fe total were made with the Atomic Absorption method; Na^+ and K^+ by flame photometry. The anions F^-, Cl^-, Br^-. HPO_4^-, NO_3^-, NO_2^- and SO_4^{2-} were analysed by the DIONEX ion chromatography method.

The mineralogical analyses were made by DAT, RDX and optical methods, from samples taken at 0.50-0.50 m intervals also. The petrographic study on consolidated samples was made by optical microscopy.

3. RESULTS AND DISCUSSIONS

The results of the mineralogical analyses are on the column of Fig.1, where the corresponding water analyses (mean values) are also. (The microcline was detected only by the optical microscopy).

As it can be observed, about till a depth of more or less 1.50 m, the chemical composition of water cannot be correlated with the mineralogy because there the influence of climatic conditions is more important. It is shown in a previous work (Szikszay et al, 1987) that the evaporation-line at the site is situated at a depth, varying between 0.50-1.50 m. In another paper (Szikszay et al., in print), it was also shown that the high

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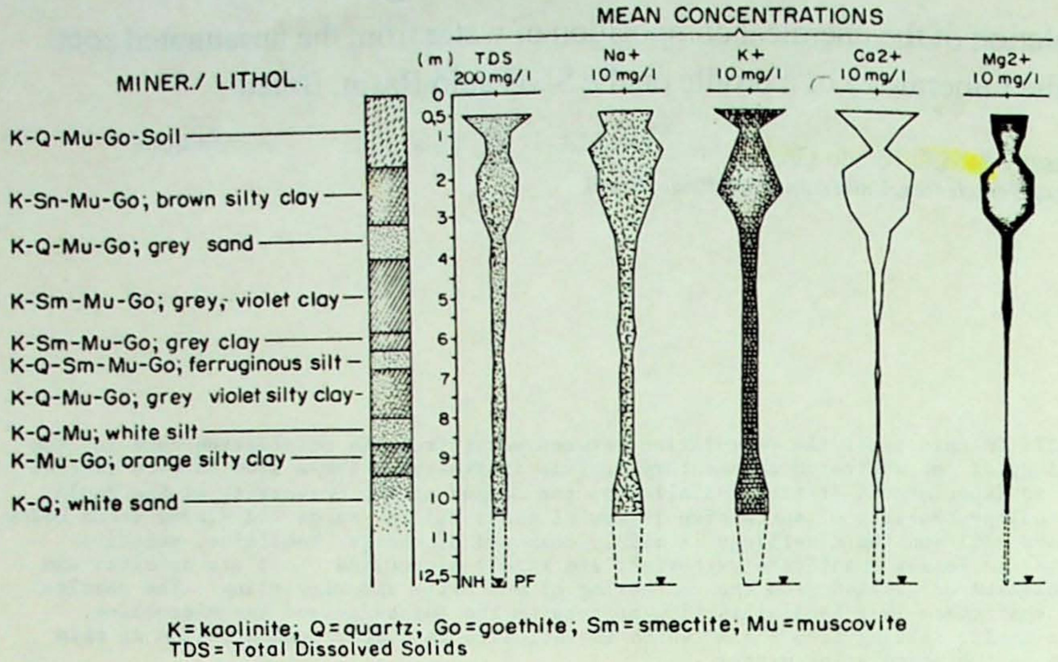


Figure 1. Mineralogical composition of the profile and concentration of Na^+, K^+, Ca^{2+}, Mg^{2+} and TDS in the waters.

concentrations of constituents in water in the upper part of the unsaturated zone, are related to successive processes of evaporation-infiltrations.

Therefore, the correlation of water from the unsaturated zone and mineralogy of the profile can be treated only beginning from a certain depth.

The chemical composition of the percolating solutions is, at the same time, cause and consequence of weathering evolution of minerals. Thus, being the minerals in equilibrium with the geochemical and physical-chemical conditions of the surroundings (water), there would not be any evolution. But if this equilibrium does not exist, then there would be a mineralogical evolution with chemical modifications, which would be reflected in the chemical composition of the waters. The waters would show gains in elements leached out from the surroundings and also losses which eventually would take part in new mineral phases.

Considering that in the solutions, the pH and the ion concentrations generally and in this case specially, the SiO_2, Na^+, K^+ and Ca^{2+} define the equilibria of the mineralogical solutions, phase-diagrams of $\log|K^+|/|H^+|$, $\log|Ca^{2+}|/H^+|$ and $\log|Na^+|/|H^+|$ versus $\log|H_4SiO_4|$ (constructed in accordance with thermodynamic data selected by Tardy, 1969) were used (Figures 2, 3 and 4), with the objective to correlate the theoretical equilibria shown on these diagrams with the observed ones as a result of the chemical analyses of waters and of the mineralogical and petrographic studies of the profile's sediments.

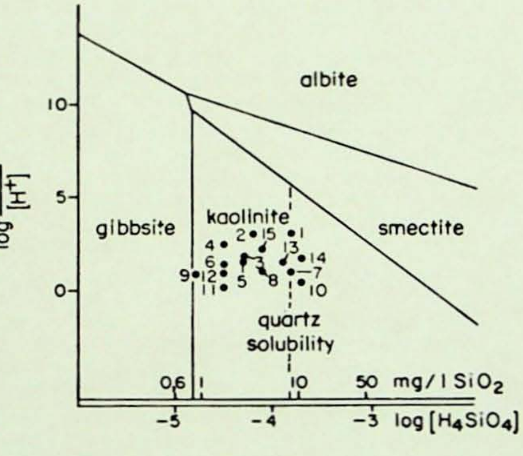
These diagrams show that the waters are always in the field of stability of the kaolinite where it is possible theoretically, the dissolution of the quartz and very slow alteration of muscovite and microcline to kaolinite. Effectively, the study of thin-sections made by the optical microscope showed those features, well known in studies of weathering. The morphology of the smectite (crystals of reduced size) do not permit to verify with the available methodology, if there is a kaolinitization process, being this however a possibility.

Thus, it can be assumed, in spite that the quantity of muscovite and microcline in these sediments is very small and its evolution to kaolinite is very slow, that the observed increase of K^+ concentration in waters from the upper part of the profile would be due to the setting free of this ion during the kaolinitization of these detritical minerals. Furthermore, it can also be observed that in the stability field of kaolinite, the part where the points of analyses are situated, is nearer to the field of more leached minerals (gibbsite) than to the less leached one (with silicium and bases: phyllosilicated 2:1), reflecting once more the leached out nature of the sediments of the São Paulo Basin together with high precipitation rates which maintain the solutions diluted.

With respect to SiO_2 present in the waters. its origin is evident from the progressive dissolution of quartz, the principal mineral at the sandy levels.

Furthermore, the observation of soil and sediment samples also showed that there is a remobilization of ferruginous products (essentially goethite) which, in spite of small quantities, is sufficient to color the material and to form typical features of remobilization in solution, such as rings of Leisegang.

The Ca^{2+}, Mg^{2+} and Na^+ have low concentrations in waters of the lower part of the profile and their origins could be related to the possible evolution of the smectite not seen on the optical microscope.



Leg: Depth of porous cups 1-4,0 m; 2-3,5 m; 4-4,0 m; 5-5,5 m; 6-6,0 m; 7-6,5 m; 8-7,0 m; 9-7,5 m; 10-8,0 m; 11-8,5 m; 12-9,0 m; 13-9,5 m; 14-10,0 m; 15-10,5 m.

Figure 2. Stability diagrams of the system $N_2O.Al_2O_3.SiO_2.H_2O$ (T=25°C,P=1 atm) showing the points corresponding to the mean values of water analyses.

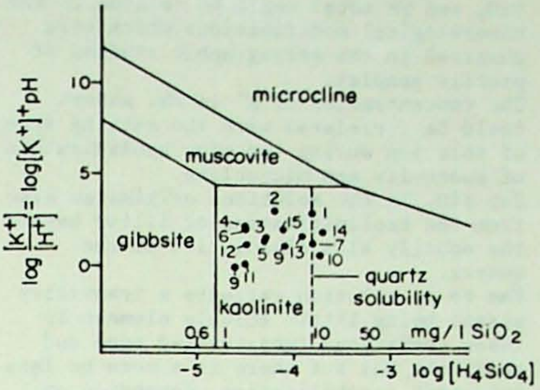


Figure 3. Stability diagram of the system $K_2O.Al_2O_3.SiO_2.H_2O$ (T=25oC, P=1 atm)

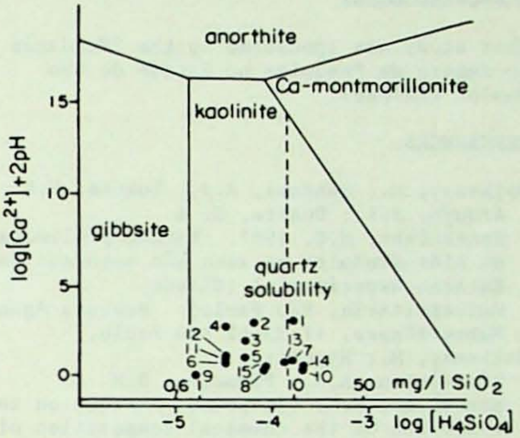


Figure 4. Stability diagram of the system $CaO.Al_2O_3.SiO_2.H_2O$ (T = 25°C. P=1 atm).

4. CONCLUSIONS

From the present study the following conclusions could be obtained:

The correlation between percolating waters and the mineralogy of the weathered sedimentary profile, in the upper part till the evaporation-line (0.50-1.50 m) is unimportant because the climate is the predominant factor showing high ion concentrations due to successive evaporation-infiltrations. Under the evaporation-line the ion concentration is low, due principally to the strong leachings peculiar of sub-tropical climates. There the concentration of K^+,

SiO_2 and Fe total could be related to the mineralogical modifications which were observed in the petrographic studies of profile samples.

- The concentration of K^+ in the waters could be correlated with the setting free of this ion during the slow kaolinization of muscovite and microcline.
- The SiO_2 in the solutions originates also from the kaolinitization of illite beyond the equally slow dissolution of the quartz.
- The Fe in solution reflects a transitory state; being little soluble element in these conditions (unsaturated zone and oxidizing Eh) but there is a more or less important remobilization, depending on the fluctuations of Eh values, causing differentiated colorings in the sediments, including feature types such as "Leisegang's rings".

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