

## PALEOENVIRONMENTS IN THE SUBTROPICAL NORTHEASTERN ARGENTINA AS DEDUCED FROM STABLE CARBON ISOTOPES COMPOSITION OF FERRALLITIC SOILS

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### INTRODUCTION

Different biological, geological and geochemical proxy indicators may contribute to the reconstruction of paleoenvironmental changes, e.g. pollen, phytolites, fossils, paleosols, etc. More recently the use of stable carbon isotopes has gained interest to infer past climatic fluctuations.

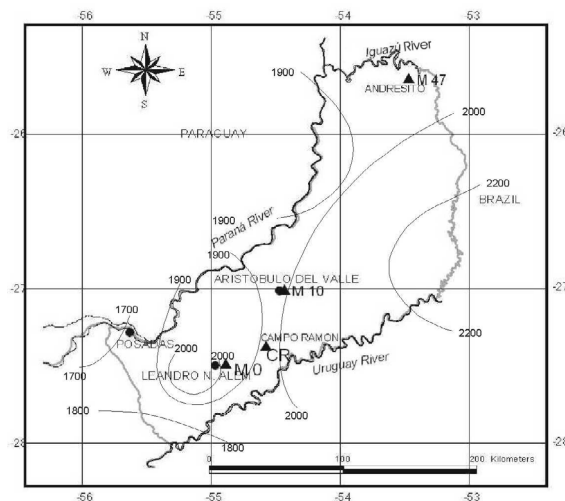
The stable carbon isotope composition of plants differs according to their photosynthetic pathway (C3, C4, and CAM).  $\delta^{13}\text{C}$  values of C3 plants like trees and almost all the plants in temperate and cold regions, range from approximately  $-32\text{‰}$  to  $-20\text{‰}$  PDB, with a mean of  $-27\text{‰}$ . In contrast  $\delta^{13}\text{C}$  values of C4 plants, adapted to conditions of higher hydric stress, range from  $-17\text{‰}$  to  $-9\text{‰}$ , with a mean of  $-13\text{‰}$  (Mariotti, 1991; Hatté and Schwartz, 2003; Pessenda et al., 2004). Isotopic fractionation depends not only on the type of vegetation but also on the plant environment, the  $\text{CO}_2$  atmospheric concentration, the temperature and on the humidity level. During litter decomposition and humification the isotopic signal of plants is transferred into the soil organic matter (SOM). Thus, the analysis of carbon isotopic composition of SOM may allow to deduce information about the environments and climatic conditions under which plants have grown in former times.

The palaeoenvironmental changes and landscape evolution of the subtropical Province of Misiones, in northeastern Argentina, has began to be analyzed only recently and some opposite interpretations have been proposed by different authors (Morrás et al., 2005 a-b). Up to now, there are no studies on the environmental evolution of this region by means of carbon isotope analyses. In contrast, there are several studies on the isotopic composition of the OM of soils in neighbouring regions of southern Brazil (vg. Desjardins et al. 1991; Pessenda et al., 2004), which provide a framework of comparison and interpretation for similar studies in subtropical Argentina.

### MATERIAL AND METHODS

The Province of Misiones is located in the northeastern extreme of Argentina, around  $27^\circ$  S and  $54^\circ$  W. The climate is subtropical humid without dry season; mean annual temperature is around  $20^\circ\text{C}$  and mean annual

rainfall increases from 1750 mm in the south to 1950 mm in the north. The present vegetation is a subtropical forest, except a narrow strip along the southern border with a savannah type vegetation. The typical soils are mainly Ultisols and, in lower proportion, Oxisols. This ferrallitic solum usually has a depth of 3 to 7 m above the weathered basalt, and a "stoneline" frequently appears in the lower part of the profiles, close to the saprolite. Stonelines are frequent in tropical and subtropical environments. Their genesis and that of the overlying material has experienced numerous interpretations, mainly under the headline "autochtony or allochtony". Referring specifically to the case of Misiones and neighbouring areas in Brazil and Paraguay, Iriondo and Kröhling (1997) postulated that the material that covers the basaltic rock and in which the red soils have developed is an eolian sediment of Upper Pleistocene age, deflated from the alluvial plains of Paraná and Uruguay rivers; the authors consider this material a "tropical loess" and named it as "Oberá Formation". On the other side, and in accordance with the traditional interpretations (Sanesi, 1965), our results suggest that the surface material and the "stonelines" have developed in situ through the weathering of the basaltic rock (Morrás et al., 2005 a-b).



**Fig. 1.** Location of the profiles under study (triangles) and mean actual precipitation

In this paper we focus on the C isotope composition of four sites along a transect from the SW to the NE in the Province of Misiones (Fig.1). Profile M0 in the southwest is located close to Leandro Alem, profile M10 is found in the central part near Aristóbulo del Valle, and the northern profile M47 was studied in Andresito. Samples were taken in high resolution from the whole solum and the underlying basaltic saprolite. Profile CR located in the proximity of Campo Ramón, between M0 and M10, includes only the upper soil horizons, but in a threefold replication.

## RESULTS

### <sup>13</sup>C VALUES OF THE SOM

According to Fig. 2 the  $\delta^{13}\text{C}$  depth function of the four profiles shows a similar trend. In the surface horizons,  $\delta^{13}\text{C}$  values are around  $-26\text{‰}$  in the profiles M47 and CR, and around  $-24\text{‰}$  in profile M10; this values are typical for C3 plants as those constituting the present forest vegetation. Approximately at one meter depth the isotopic signature shows a significant enrichment in <sup>13</sup>C, reaching  $\delta^{13}\text{C}$  values of around  $-19\text{‰}$  in CR,  $-18\text{‰}$  in M10 and M47, and  $-15\text{‰}$  in M0. This increase might be due to soil organic matter derived from C4 plants, grown under more arid conditions. In the deeper part of the profiles, above and below of the “stonelines”,  $\delta^{13}\text{C}$  values are around  $-21\text{‰}$  PDB, probably indicating a mixture of C3 and C4 plants. At higher depth, in the saprolite, the  $\delta^{13}\text{C}$  values remain constant around  $-21\text{‰}$  in M0 and M10, while in M47 the values are around  $-25\text{‰}$  which correspond more clearly to a C3 vegetation, typical for a more humid climate.

### ENVIRONMENT AND SOIL EVOLUTION

In all profiles studied we observed a progressive <sup>13</sup>C enrichment with depth from the surface A horizon to the subsurface Bt horizon in around one meter depth. The difference in the  $\delta^{13}\text{C}$  values of the A- and the Bt-horizons are higher than the about  $3\text{‰}$ , the value considered to indicate isotopic fractionation by soil-inherent processes (Mariotti, 1991; Balesdent, 1991; Krull and Skjemstad, 2003). Consequently, it can be concluded that the differences observed in the 13C/12C ratios of SOM in the upper meter of these soils are related with differences in the C isotopic composition of parent vegetation: the more negative <sup>13</sup>C values of the A horizons reflect the present forest vegetation with a prevalence of C3 plants growing under the actual humid climate, while the less negative  $\delta^{13}\text{C}$  values suggest a previous period with more C4 plants grown under somewhat drier climatic conditions with a more open savannah like vegetation. These results coincide with those obtained by Desjardins et al (1991) and Pessenda et al (2004) in soils from southern Brazil, in environments similar to that of Misiones. According to these authors, and in agreement with the results of several other authors (vg. Servant, 1981; Behling et al., 1998), the <sup>13</sup>C

enrichment observed t in the Bt horizons of our soils might be related with a drier paleoclimate.

On the other hand, the intermediate  $\delta^{13}\text{C}$  values (around  $-21\text{‰}$ ) recorded in the lower B horizons and around the “stoneline”, are more difficult to interpret (Schwartz, 1991). Firstly these results may indicate organic matter inputs from a vegetation dominated by plants of the C3 photosynthetic pathway in mixture with C4 plants; this could be the case of an open forest in a drier climate, as has been interpreted for ferrallitic soil profiles in the state of Sao Paulo, Brazil (Pessenda et al, 2004). A second interpretation is the one made for similar values observed in soils in southern Brazil (Desjardins et al., 1991) and in the Congo (Schwartz, 1991), which have been related with transitional environments, specially when a forest is encroaching a savannah; in this case the  $\delta^{13}\text{C}$  would be the mean of two different vegetations, replacing successively one to the another in connection with paleoclimatic variations. Thirstly, it should be considered that the ecophysiological conditions, and particularly the utilization of water by plants, control the  $\delta^{13}\text{C}$  of photosynthetized products: the  $\delta^{13}\text{C}$  of C3 plants is more sensitive to environmental changes than C4 plants. This means that intermediate  $\delta^{13}\text{C}$  values measured in depth may correspond to the same forest vegetation living today, but under a past different environment, for example under colder and drier conditions (Balesdent, 1991).

In our case we would like to call the attention on another factor of incertitude to interpret these intermediate isotopic values, and that apparently has not been considered by other authors, which is the mixing effect of soil fauna. As it is known, in subtropical and tropical environments the activity of termites is strong and would have an important role in soil profile development (Johnson et al., 2005). Thus, a single succession from an ancient humid forest environment to a more recent drier savannah may result in intermediate 13C/12C ratios as those observed in deeper horizons in Misiones profiles.

Concerning the C isotopic composition in the saprolite (C horizons), profiles M0 and M10 show similar or a little bit more negative  $\delta^{13}\text{C}$  values than those measured in deeper B horizons; in turn, in profile M47 the values in the saprolite are much more negative, equalizing those in upper A and Bt horizons. These results seems to indicate that the present climatic differences between the south and the north of Misiones have also existed and possibly were even more pronounced in former times, before the aridization registered in the upper part of the profiles.

Consequently, our results are not in agreement with those of Iriondo and Kröhling (1997) who consider the stonelines, appearing several meters down in the profiles, as the evidence for aridization during the Late Pleistocene/Early Holocene, and all the materials above it as eolian sediments. In addition, our first radiocarbon dates let assume that the  $\delta^{13}\text{C}$  shift to more positive values in about 1m soil depth correlates with a climatic deterioration between 7-3 ka BP.

Besides the fact that the isotopic signature around the stonelines seems not to correlate with climatic conditions favoring accelerated erosion of a former soil, gravel accumulation as a stoneline, and a later eolian sedimentation several meters thick above the stonelines, other field and laboratory evidences obtained up to now suggest an autochthonous origin of the ferrallitic mantle and the stonelines, in Misiones. Among these are: 1) the clay fraction shows a gradual mineralogical variation from the saprolite up to the surface, given by a decrease of kaolinite and a parallel increase of chloritic minerals; 2) the magnetic susceptibility shows a gradual increase from the saprolite towards the surface; 3) the geochemical data and several homogeneity indices do not show a discordance between the saprolite and the upper part of the soils. These results (fig. 3) suggest that all the material above the saprolite is the result of in situ weathering of the basalt. 4) The granulometric data show a gradual increase of clay and silt fractions from the surface to the middle part of the soil profiles, and then a progressive decrease towards the base of the saprolite. This result reflects the process of illuviation typical for Ultisols together with a weathering process of the crystalline rock. 5) The gravels are not restricted to the stonelines, suggesting that they are not related to an accumulation on a paleosurface. 6) The exoscopy of quartz grains from the sand fraction do not show evidences of eolian transport, on the contrary clear traces of chemical dissolution and of quartz recrystallisation appear.

## CONCLUSIONS

-The depth function of stable carbon isotopes in ferrallitic soils of Misiones, allows to differentiate the present humid climatic period with a forest vegetation with C3 plants, from a previous one with plants of the C4 type that should developed under conditions of hydric stress in a savannah environment. These last conditions have probably existed in Misiones during the LGM and the first half of the Holocene, as it is registered by several authors in southern Brazil. But according to our radiocarbon analyses the climatic deterioration responsible for the increase of the delta 13C values occurred during the mid Holocene (7-3 ka BP).

-In the lower part of the profiles, the measurement of  $\delta^{13}\text{C}$  gives intermediate values that are more difficult to be explained. Anyway, and in accordance with the interpretations made for similar situations, it is considered that these  $\delta^{13}\text{C}$  values result from a vegetation dominated by C3 plants in an open forest and under intermediate climatic conditions between the two both registered in the upper part of the soils.

-The differences in the  $\delta^{13}\text{C}$  values observed in the saprolite between the profiles M0 and M10 in the meridional part of Misiones with the values in the profile M47 in the septentrional extreme, suggest a gradient of paleoprecipitations equivalent to the present one, with an increase of rains from the SW to the NE.

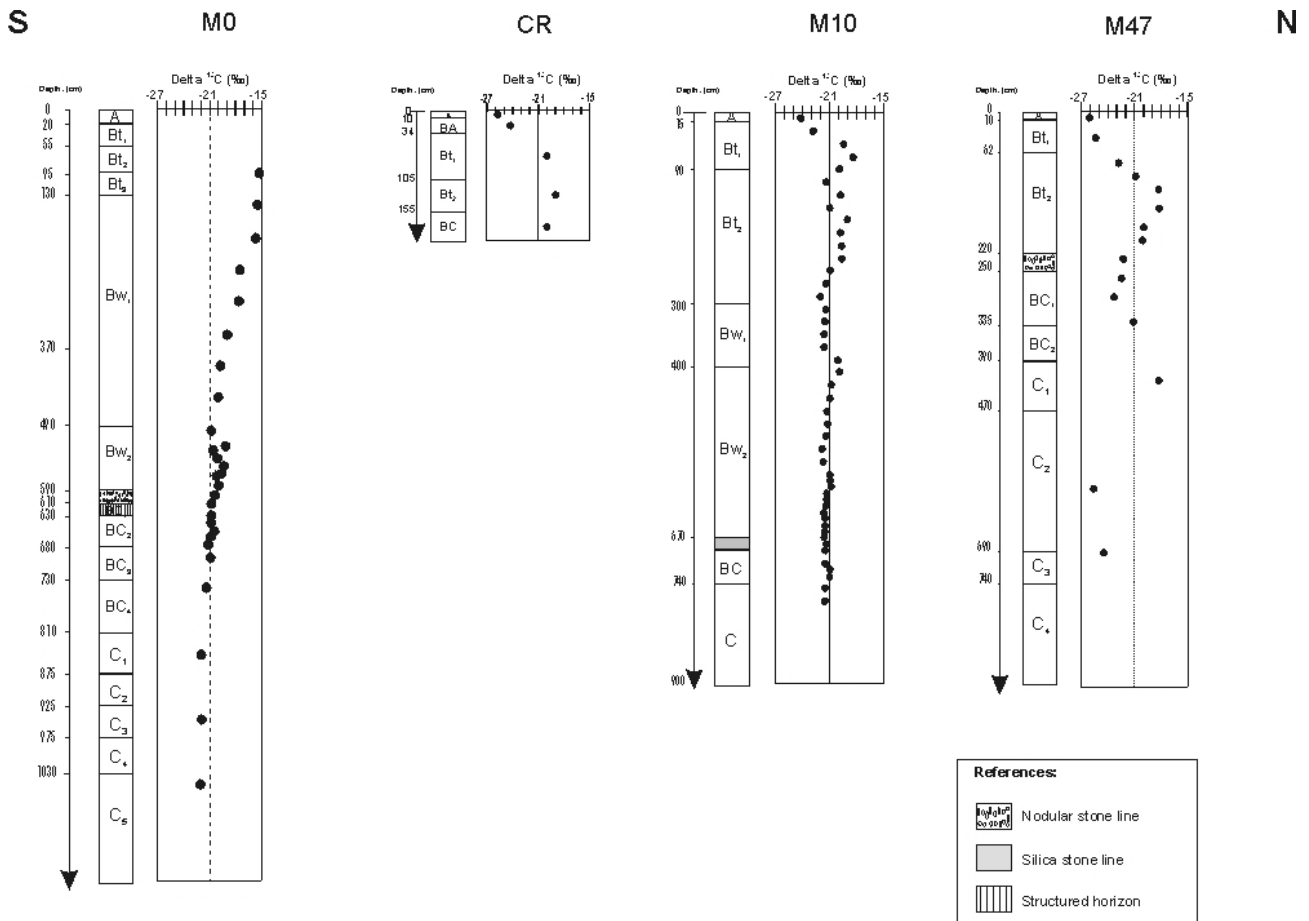
-In the vicinity of the stonelines our proxies do not indicate a C4 grass vegetation, a prerequisite for accelerated denudation, accumulation of gravels on a paleosurface and a later eolian sedimentation, that would be linked to the LGM as has been proposed by other authors. Besides, and though eolian inputs might not be excluded completely, several other field and analytical results also suggests an autochthonous origin for the stonelines and the upper part of the solum.

## REFERENCES

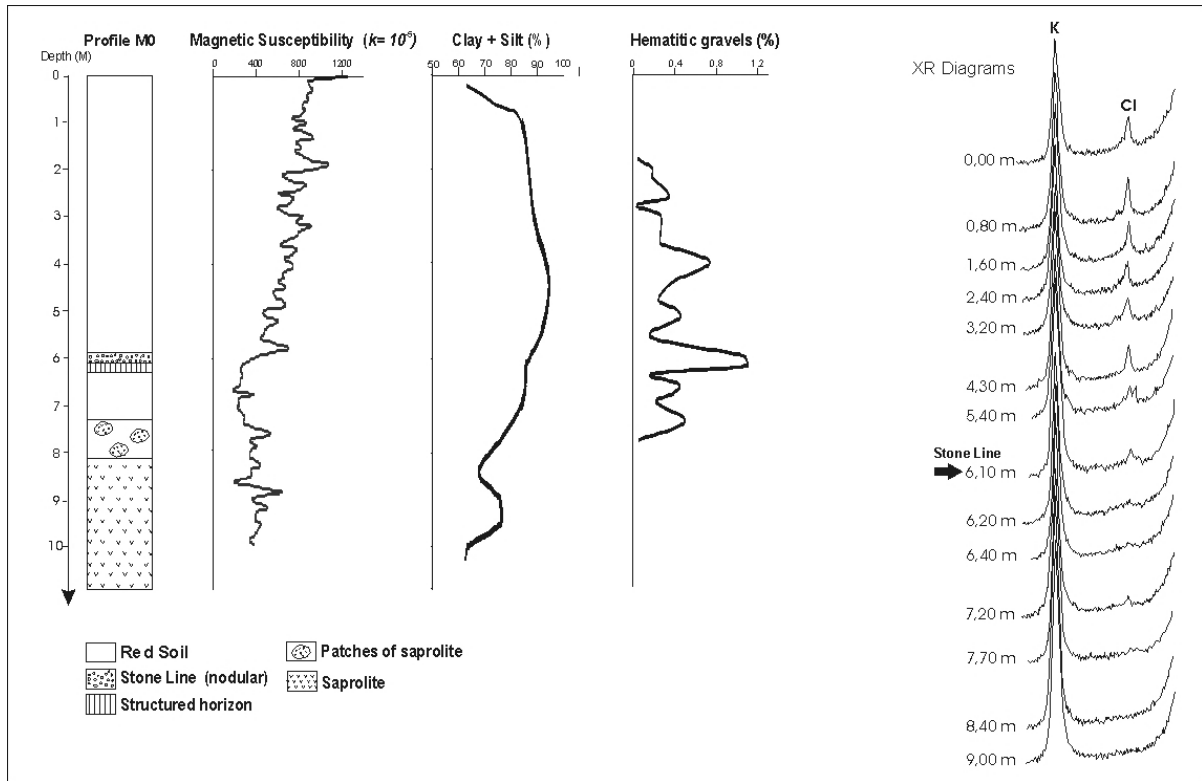
- Balesdent, J., 1991. Estimation du renouvellement du carbone des sols par mesure isotopique  $^{13}\text{C}$ . Précision, risque des biais. Cah. ORSTOM, sér. Pédol., XXVI (4): 315-326
- Behling, H., Lichte, M. and Miklós, A., 1998. Evidence of a forest free landscape under dry and cold climate conditions during the Last Glacial Maximum in the Botocatu region (Sao Paulo State), Southeastern Brazil. Quaternary of South America and Antarctic Peninsula, 11, 99-110.
- Desjardins, T., Andreux, F., Volkoff, B. and Cerri, C., 1991. Distribution de l' isotope  $^{13}\text{C}$  dans des sols ferrallitiques du Brésil. Cah. ORSTOM, sér. Pédol., XXVI (4): 343-348
- Hatté, C. and D. Schwartz, 2003. Reconstruction of paleoclimates by isotopic analysis: What can the fossil isotopic record tell us about the past life of the past environments?. *Phytochemistry Reviews* 2: 163-177
- Iriondo, M. and Kröhling, D., 1997. The tropical loess. Proc. 30<sup>th</sup> International Geological Congress, (An Zhisheng et al., Eds.), Vol. 21, p. 61-77
- Johnson, D., Domier, J. and Johnson, D.N., 2005. Animating the biodynamics of soil thickness using process vector analysis: a dynamic denudation approach to soil formation. *Geomorphology* 67, 23-46
- Krull, E. y J. Skjemstad, 2003.  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  profiles in  $^{14}\text{C}$ -dated Oxisol and Vertisols as a function of soil chemistry and mineralogy. *Geoderma* 112, 1-29
- Mariotti, A., 1991. Le carbone 13 en abondance naturelle, traceur de la dynamique de la matière organique des sols et de l'évolution des paléoenvironnements continentaux. Cah. ORSTOM, sér. Pédol., XXVI (4): 299-313
- Morrás, H., Moretti, L., Piccolo, G. and Zech, W., 2005-a. New hypotheses and results about the origin of stonelines and subsurface structured horizons in ferrallitic soils of Misiones, Argentina. 2<sup>nd</sup> Assembly of the European Geosciences Union, Vienna, Geophysical Research Abstracts, Vol. 7, 05522, 2005
- Morrás, H., Moretti, L., Piccolo, G. and Zech, W., 2005-b. Nueva hipótesis acerca del origen de las líneas de piedra y los horizontes estructurados subsuperficiales en los suelos ferralíticos de Misiones, Argentina., *Actas XVI Congreso Geológico Argentino, La Plata, septiembre 2005*, pp.
- Pessenda, L., Gouveia, S., Aravena, R., Boulet, R. and Valencia, E., 2004. Holocene fire and vegetation changes in southeastern Brazil as deduced from fossil charcoal and soil carbon isotopes. *Quaternary International* 114, 35-43
- Sanesi, G., 1965. I suoli di Misiones. *Accademia Italiana di Scienze Forestali*, 343 p.
- Schwartz, D., 1991. Intérêt de la mesure du  $^{13}\text{C}$  des sols en milieu naturel équatorial pour la connaissance des aspects pédologiques et écologiques des relations savane-forêt. Exemples du Congo. Cah. ORSTOM, sér. Pédol., XXVI (4): 327-341

## RESUMEN

La Provincia de Misiones en el NE de Argentina, se caracteriza por un clima subtropical y suelos ferralíticos. Con el propósito de mejorar el conocimiento sobre los cambios ambientales y la evolución de suelos en el área, se analizó la composición isotópica del C de la materia orgánica de cuatro perfiles de suelo a lo largo de una transecta desde el S al N de Misiones. Los valores obtenidos de los isótopos estables del carbono en relación con la profundidad permiten diferenciar el clima húmedo actual con vegetación de tipo C3 ( $\delta^{13}\text{C}$  alrededor de  $-25\%$ ), de una precedente con plantas de tipo C4 ( $\delta^{13}\text{C}$  entre  $-15$  y  $-19\%$ ) que se habría desarrollado en un ambiente de sabana; de acuerdo a los análisis radiocarbónicos el deterioro climático responsable por este incremento de  $\delta^{13}\text{C}$  ocurrió durante el Holoceno medio (7-3kaBP). En la parte inferior de los perfiles, los valores de  $\delta^{13}\text{C}$  son intermedios, interpretándose los como el resultado de una vegetación con dominancia de plantas C3 bajo condiciones climáticas intermedias entre las dos registradas en la parte superior de los perfiles. Las diferencias de  $\delta^{13}\text{C}$  observadas en el saprolito entre los perfiles situados al S y al N de Misiones sugieren un gradiente creciente de paleoprecipitaciones en la misma dirección. Alrededor de las líneas de piedra los datos no indican una vegetación de tipo C4, que sería un prerrequisito para el establecimiento de procesos de erosión, acumulación de gravas y una posterior sedimentación eólica que pudieran relacionarse con el UMG tal como ha sido propuesto por otros autores. Si bien los aportes eólicos no pueden excluirse completamente, diversos otros resultados analíticos y de campo sugieren el origen autóctono de las líneas de piedra y de la parte superior del solum.



**Fig. 2.**  $\delta^{13}\text{C}$  variations with depth in the four profiles studied along the Province of Misiones



**Fig. 3.** Some analytical results from profile M0: Magnetic susceptibility (in volume), granulometric data, distribution of the hematitic gravels with depth and clay mineralogy (k=Kaolinite; Cl=Chloritic minerals)