# Land erosion and associated evolution of clay minerals assemblages from soils to artificial lakes in two distinct climate regimes in Portugal and Brazil

R. FONSECA[1],*, F. J. A. S. BARRIGA[2] AND K. TAZAKI[3]

[1] *Department of Geosciences, University of Évora, 7002-554 Évora, Creminer LA/ISR, Faculty of Sciences, University of Lisbon, Campo Grande, 1794-016 Lisbon, Portugal,* [2] *Department of Geology and Creminer LA/ISR, Faculty of Sciences, University of Lisbon, Campo Grande, 1794-016 Lisboa, Portugal, and* [3] *Department of Earth Sciences, Faculty of Science, Kanazawa University, Kakuma, Kanazawa, Ishikawa, 920-1192, Japan*

ABSTRACT: Given that reservoirs contain most of the leached materials from soils, we have studied the sediments accumulated in the bottom of two groups of reservoirs developed under different climatic conditions and thus with contrasting rates of weathering/erosion regimes. Through detailed comparative study of clay minerals of the parent rocks and soils with the clay fractions of the dam sediments, we have concluded that, during cycles of erosion-transport-deposition, the leached materials have complex transformation mechanisms, making them much more active in the environment. All clay-mineral groups are well represented in the reservoir sediments, including abundant mixed-layer and partly disordered minerals. Moreover, the sediments are nutrient-rich and potentially useful as agricultural fertilizers and hence in reversing the declining soil productivity in some regions.

Due to over-erosion in soils worldwide, the finer particles, which contain the nutrition elements much needed for sustainable organic productivity, are easily washed away and soils become coarse-textured, deficient in a host of components and they lose their fertility (Fonseca, 2002; Fonseca *et al.*, 2003).

The presence of an artificial lake in a river controls the suspended sediment load carried (Berner & Berner, 1996). Since the boom of dam construction in the early 1950s, there are significant differences between the volume of matter eroded and the volume of sediment discharged into the oceans, because much of the material eroded from uplands is deposited in the aforementioned reservoirs, without reaching the sea (Hay, 1998). Reservoir lakes are characterized by (1) low hydrodynamics, (2) thermal stratification, (3) high temperatures and, above all, (4) reducing conditions. Once deposited, the fine-grained sediments undergo very complex transformations of both a chemical and a physical nature (ionic exchange, cationic fixation, degradation of mineral structure). These transformations, coupled with those occurring during the earlier stages of soil weathering and particle transport, generate marked differences between the accumulated sediments and their parent materials, the soils of the drainage basins.

* E-mail: rfonseca@uevora.pt

The rapid accumulation of erosion products in reservoirs causes a number of problems, including filling of the reservoir, thereby rendering it useless, and changing the properties of the reservoir water.

Although there have been many studies on soil erosion worldwide, there are very few on dam-reservoir sediments. The purpose of the present study is to establish a link between the two, through characterization of the mineralogical transformations of clay minerals, as these are the particles more susceptible to weathering, from over-eroded soils to their deposition in the bottom of large artificial lakes.

The present study is part of a broader one which aims to evaluate the possibility of removing reservoir sediments and returning them to the soils of the drainage areas. The use of nutrient-rich sediments in agriculture might help to solve the declining soil productivity in some regions. Additionally, the removal of sediments from the reservoirs will certainly improve the water quality and thereby the quality of life in many regions dependent on surface-water storage.

## GENERAL CHARACTERIZATION OF THE SELECTED DAM RESERVOIRS

We selected two distinct groups of dam reservoirs, developed under different climatic conditions and thus with contrasting types and rates of weathering/erosion. Their drainage basins are also subject to different external factors that control the sedimentation into the reservoirs (lithology/geochemistry of influenced areas, geomorphology, soil characteristics, human impact). Group 1 is of Portuguese reservoirs (Maranhão, Monte Novo and Divor), under a Mediterranean climate and group 2 comprises a Brazilian reservoir (Passo Real), under a sub-tropical climate. In both groups, the reservoirs are located in active agricultural areas free of polluting industries and they are old enough to have large accumulations of sediments, and to have distinct hydrological and morphological characteristics.

### Climatic, hydrological and geomorphological conditions of the drainage basins of reservoirs

*(1) Portuguese reservoirs*. Located in southern Portugal (Alentejo region), the reservoirs belong to the hydrological systems of the Tagus (Maranhão and Divor) and Guadiana rivers (Monte Novo). They are situated in a peneplain slightly undercut by the drainage network. The Mediterranean climate, characterized by a hot, dry summer and a rainy winter (Csa in the Koppen classification), leads to greater sedimentation rates from autumn to spring, as a consequence of the erosion caused by rain. The settling of most fine-grained particles takes place during the summer, when hydrodynamic activity is less intense.

*(2) Brazilian reservoir*. Passo Real is located in Rio Grande do Sul, the southernmost Brazilian state and belongs to the hydrological system of Guaíba. This reservoir is located at the southern margin of the Basaltic Plateau, a monoclinal unit which dominates the northern half of the State, composed of sequential emissions of cretaceous basaltic-tholeitic rocks (Menegotto & Gasparetto, 1987). The relief forms are uniform, regarded as hills with gentle slopes and rounded shapes. The sub-tropical climate of this reservoir is characterized by homogeneous rain distribution throughout the year. These conditions lead to a much greater intensity of rock and soil weathering, followed by extreme leaching of soluble elements.

### Lithology of the drainage basins

The Portuguese reservoirs consist of a remarkable geological diversity. The Maranhão drainage area includes a Cenozoic sedimentary cover over Palaeozoic and Precambrian formations (Fig. 1). This basement includes a wide variety of metasediments (mostly shales, but also pelitic schists, greywackes, quartzites, conglomerates, carbonate rocks), metavolcanic sequences ranging in composition from acid to basic, and a large intrusive massif (geochemically diverse granitic rocks and mafic and ultramafic intrusive bodies). The Cenozoic sedimentary cover is mainly detrital (Oliveira *et al.*, 1992). The geology of the smaller Monte Novo and Divor systems is less diverse, composed mainly of schists with some basic and acid volcanics and intrusive acid rocks (tonalitic and granitic), and scarce zones of Miocene cover (shales, conglomerates and carbonate rocks; Oliveira *et al.*, 1991, 1992).

The sources of the sediments of the Brazilian reservoir are far more homogeneous: tholeiitic basalts associated with fewer zones of felsic volcanics (Serra Geral Formation) and detrital cover (Tupanciretã Formation) (Peate *et al.*, 1992; Favilla *et al.*, 1998) − Fig. 2.
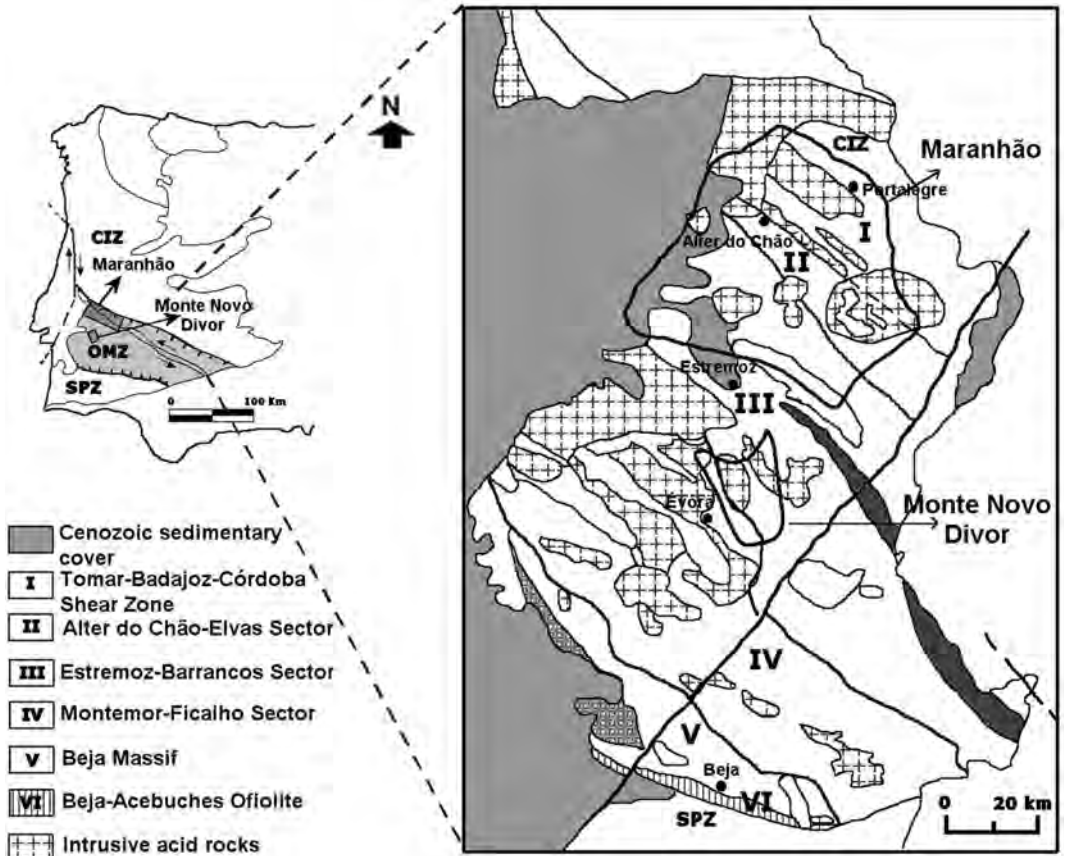
F<sub>IG</sub>. 1. Location of the drainage basins of the Maranhão, Monte Novo and Divor reservoirs in the tectono-stratigraphic units of the Ossa Morena Zone (OMZ) in Portugal. Adapted from Oliveira *et al.* (1991).

*Characterization of soils from drainage basins*

The drainage area of the Portuguese reservoirs contains as the dominant soil group weakly developed soils resulting from *in situ* weathering of various rock compositions or from soil-forming processes such as leaching or argilluviation (related to clay-enrichment) – rodochromic Luvisols and ocric Luvisols. In the steepest slopes, Cambisols mainly occur.

The southern Brazilian climatic conditions and the high water/rock ratio over a mainly basaltic lithology provide soil units characterized by thick surface layers enriched in fine-grained particles – Ferrasols and Cambisols, and less commonly, Podzols.

MATERIALS AND METHODS

*Sampling of sediments in dam reservoirs*

The sediments were sampled and mapped in the reservoirs following sampling grids (initially with regularly spaced nodes) adjusted to the position and importance of the various water streams that feed the reservoirs (60 points in Maranhão, 13 in Monte Novo, 10 in Divor; 17 in Passo Real). The samples were collected using either a Shipeck dredge or a modified Van Veen dredge, from variable depths: 1.5–40 m in Maranhão, 1.5–30 m in Monte Novo, 1.5–18 m in Divor and 4–47 m in Passo Real. In Portugal, sampling took place during the two most representative periods in the
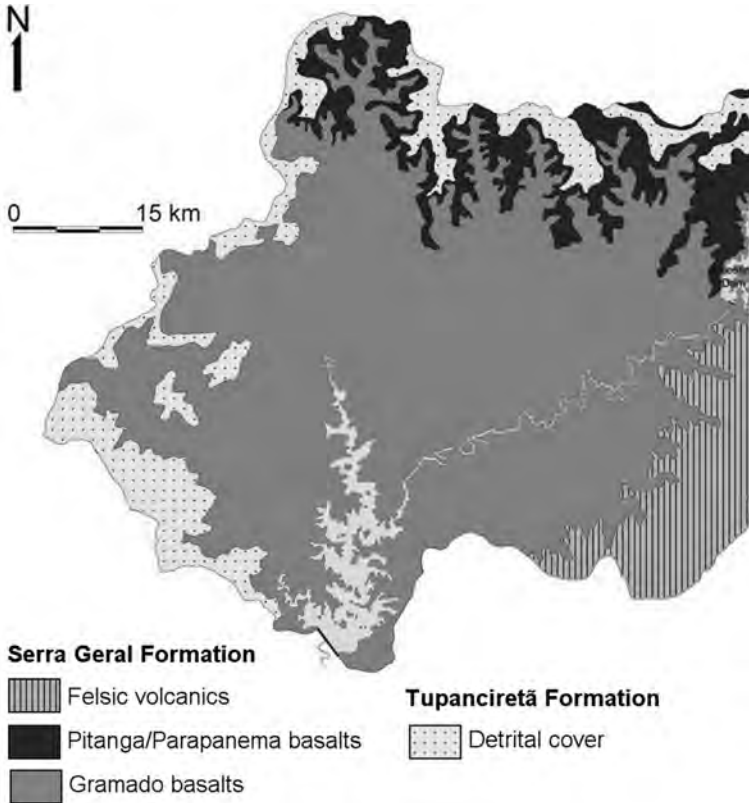
FIG. 2. Geological setting of the Passo Real drainage basin.

annual cycle, at the same locations (February and September), and in Brazil, sampling took place during February only.

## Mineralogical analysis

The clay minerals from the clay fraction (<2 μm) of the sediments were examined by X-ray diffraction (XRD) using a Philips PW 1710 diffractometer with automatic slit and Cu-$K\alpha$ radiation at 40−50 kV, 30−40 mA. The XRD patterns were collected in the 2−50º2θ range and counts were recorded at 0.02º2θ intervals.

The clay fraction (<2 μm) was extracted by normal centrifugation techniques after removal of the organic matter by hydrogen peroxide treatment. Separate aliquots were saturated with Mg, K and Li (only performed on the Portuguese samples, due to the large variety of clay minerals) by methods adapted from Thorez (1976), Ransom *et al.* (1988) and Moore & Reynolds (1997), and oriented aggregates were produced by pipetting a clay suspension on glass slides to eliminate mineral segregation. The natural and Mg-K-saturated samples were air-dried, solvated with ethylene glycol (EG) and heated to 550ºC. The Li-saturated sample was submitted to the Greene-Kelly (1955) test − heating to 300ºC for 12 h followed by EG treatment. In the mineralogical study of sediments from the Brazilian reservoir, Passo Real, X-ray fluorescence (XRF) was used as a complementary technique.

Clay mineral identifications and semi-quantifications were based on methods described by Brown & Brindley (1980), Brindley (1981), Velde (1995), Moore & Reynolds (1997) and S. Hillier (pers. comm.). The identification and characterization of minerals was attained through the direct comparison of peak positions and intensities in patterns obtained from various treatments (air-dried, EG solvation, heat treatment, Mg-K-Li-saturation). Semi-quantitative results were achieved by estimation of the areas of certain peaks in EG-solvated patterns (as proposed by Moore & Reynolds, 1997).

In mixed-layered structures, peaks were chosen that have the least possible interference from discrete phases and a position independent of chemical composition. The relative proportions of each mineral phase normalized to 100% were estimated through the integrated intensity of its reflections from glycol-treated samples. This parameter was calculated, dividing each peak area (calculated by multiplying peak height by peak width at half height) by intensity calibration factors taken from Moore & Reynolds (1997) and S. Hillier (pers. comm.). The mineral intensity factors (MIF) for each mineral group were based on the unit intensity for the $I_{003}$ reflection, selected as the base of normalization.

## RESULTS

### Weathering mineralogy of rocks and soils from the drainage areas

*(1) Portuguese reservoirs.* Studies undertaken by Abreu (1986), Vieira e Silva (1990) and Fonseca (2000) on the mineralogy and geochemistry of the weathering products from altered rocks and related soils from the drainage basins of these reservoirs indicate, independent of the lithology, the clear predominance of smectites (beidellite, nontronite, montmorillonite) in the finest fractions, illites and kaolinites in the coarsest fractions and chlorites and vermiculites in the intermediate-size fractions. Mixed-layer species such as illite-smectite (I-S) and

TABLE 1. Weathering mineralogy of rocks from drainage basins of Portuguese reservoirs (Maranhão, Monte Novo and Divor). The underlined words represent the major minerals in each lithotype. Mineralogical identification adapted from Abreu (1986), Vieira e Silva (1990) and Fonseca (2000).

| Major groups of rocks | Mineral constituents (in order of decreasing weathering vulnerability) | Major alteration products (weathering rock profiles/ soil) | Major groups of rocks | Mineral constituents (in order of decreasing weathering vulnerability) | Major alteration products (weathering rock profiles/ soil) |
|---|---|---|---|---|---|
| Granite | Amphibole <u>Plagioclase</u> <u>Biotite</u> K-feldspar <u>Quartz</u> | Kaolinite Illite; Illite-smectite Smectite (beid.+ mont.) Al-vermiculite | Gneiss | Biotite <u>Feldspar</u> <u>Quartz</u> | Low-charge vermiculite Kaolinite Illite Goethite |
| Granodiorite | <u>Biotite</u> <u>K-feldspar</u> <u>Quartz</u> | Mica-vermiculite Kaolinite | Marble | <u>Carbonates</u> <u>Ca Mg oxides</u> Chlorite | Kaolinite Illite-smectite Fe oxides |
| Gabbro | Olivine <u>Pyroxene</u> <u>Amphibole</u> <u>Plagioclase</u> Oxides | Smectite (beid., nontr.) Al-vermiculite; Fe-vermiculite Kaolinite Fe oxides | Basic metavolcanites | <u>Olivine</u> <u>Glass</u> Pyroxene Plagioclase | Smectite (saponite, beidellite) Halloysite Fe oxides |
| Sericite-chlorite schist | Amphibole Biotite K-feldspar Chlorite | Vermiculite Vermiculite-smectite (Fe) Chlorite-smectite | Ultrabasic rocks (serpentine) | <u>Pyroxene</u> <u>Serpentine</u> <u>Talc</u> Chysotile <u>Chlorite</u> | Fe-smectite (nontronite) Chlorite Chlorite-vermiculite Oxides/Fe hydroxides |
| Quartz-schist | Biotite K-feldspar Quartz Chlorite | Vermiculite Illite Kaolinite Chlorite | Amphibolites | Olivine Plagioclase <u>Amphibole</u> | Vermiculite Fe-smectite Kaolinite |

chlorite-vermiculite (Ch-V) are frequently associated with the above individual clay minerals. Table 1 summarizes the major groups of clay minerals formed through transformation or neoformation processes of the main primary mineral phases.

*(2) Brazilian reservoirs.* According to the studies of Menegotto & Gaspareto (1987), Polii & Roeser (1987) and Schenato *et al.* (1995), it is possible to synthesize the set of clay minerals produced in the weathering profiles of rocks from the major geological unit, Serra Geral Formation (which takes up >90% of the setting area) and in the soils overlying them, as shown in Table 2.

The main mineralogical components of the clay-size fraction of the Tupanciretã Formation are shown in Table 3.

## Mineralogical characterization of bottom sediments of the reservoirs

*(1) Clay minerals in the Portuguese reservoirs.* In the Portuguese reservoirs, most sediments have strong first-order reflections with similar basal spacing, differing only in terms of the intensity of peaks and, in a few cases, in terms of their breadth (width of the diffraction peak at half its height above background) and shape. These XRD patterns indicate high mineralogical homogeneity of the clay fraction of sediments, independent of the reservoir and the sampling period. The differences that do occur are restricted to relative contents, grain size, crystallinity index and nature of cations in the mineral structure.

Considering the higher-order reflections at the low-angle diffraction region, under most diagnostic treatments, most XRD patterns show the following: (i) air-dried samples produce a well defined peak at

TABLE 2. Weathering mineralogy of rocks from Serra Geral Formation, dominant lithology in the setting area of Passo Real reservoir. For each mineral phase, the most abundant secondary products are underlined. Mineralogical identification adapted from Menegotto & Gasparetto (1987), Polli & Roeser (1987) and Schenato *et al.* (1995).

| Serra Geral Formation (Major groups of rocks) | Mineral constituents (in order of decreasing weathering vulnerability) | Major alteration products (weathering rock profiles/soil) |
|---|---|---|
| Basalts | Olivine Pyroxene Glass Plagioclase Magnetite K-feldspar | Smectite Amorphous Fe, Al Goethite Kaolinite (fair) |
| Ryolite | Calcite Pyroxene Plagioclase Hornblende K-feldspar Magnetite | Illite Kaolinite Goethite Smectite Amorphous mat Chlorite-vermiculite |
| Volcanic glass | Pyroxene Glass Plagioclase Magnetite | Smectite (montm.) Kaolinite Amorphous material Goethite (fair) |

14−15 Å, followed by less intense peaks at 10 and 7−7.2 Å; (ii) in EG-solvated preparations, the superimposed 14−15 Å peak separates into two, one at 17 Å and another at the original 14 Å. The reflections at 10 and 7−7.2 Å are kept; (iii) heating

TABLE 3. Major mineralogical components of the clay fraction of Tupanciretã Formation rocks. Mineralogical identification adapted from Ramos & Formoso (1975) and Moore & Reynolds (1997).

| Detrital formation of Tupanciretã (Major groups of rocks) | Major minerals in the clay size-fraction |
|---|---|
| Conglomerates Conglomeratic sandstones Clayey sandstones | Illite Chlorite Illite-smectite Chlorite Smectite Corrensite (0.5 Ch/0.5 S) |

at 550ºC collapses all the referred peaks and increases the intensity of a peak near 10 Å significantly. In some samples from Maranhão and Monte Novo reservoirs one can detect a weak peak or broad reflection at $11-12$ Å.

The behaviour of the reflections under natural conditions and under Mg-, K-, Li-saturation shows a highly diverse set of clay minerals represented by illite, smectite, chlorite, kaolinite, vermiculite and interstratified structures with distinct layers.

The XRD patterns of three samples from Maranhão, Monte Novo and Divor illustrate the changes produced by natural sample treatment procedures and provide the basis for the initial qualitative identification of the phases present (Fig. 3).

In most sediments, the standard treatment of natural specimens produces asymmetric peaks with $d_{001}$ greater than normal, often associated with weak and broad diffraction bands or shoulders on strong first-order reflections and the presence of different breadths and irrational spacings on the same set of 001 peaks denotes that most clay minerals, though they can occur as discrete species, often correspond to mixed-layered structures (Fig. 4).

The Mg-, K- and Li-saturation of samples enhanced the distinction between minerals having similar $d$ spacings, such as smectite, vermiculite and chlorite at 14 Å, and permitted definition of several chemical and structural characteristics as follows (Fig. 5):

*(a) Identification and characterization of smectite*. The distinction of smectite from vermiculite and chlorite was based on the expansion of the 001 reflection to $17-18$ Å upon glycolation of a Mg-saturated sample, and on the collapse to 10 Å, producing a diffraction pattern similar to that of illite upon K-saturation under air-dried conditions or after heating at 500ºC. At Maranhão, most smectitic minerals have a strong, well defined, symmetrical or near symmetrical but broadened reflection and the harmonic reflections at 8.5 Å (002), 5.7 Å (003) and 3.4 Å (005) are often detected as weak, broad peaks or even shoulders on basal reflections of other minerals (Fig. 5). The predominance of Ca as an interlayer cation is denoted by the $d$ spacing values in air-dried and glycolated samples and by the shifting of $S_{001}$ upon Mg saturation.

In a large number of samples, the contraction of the first-order reflection after K saturation in air-dried conditions, giving a broad band near $10-11$ Å, allows an accurate identification of high-charge smectites (originating from the transformation of other minerals, namely illite) – see Fig. 5. Under the same treatments, the occurrence of a peak or broad reflection at $12-12.5$ Å denotes the presence of low-charge smectites or Fe-smectites (authigenic, formed from the weathering of augite, hornblende or feldspars – see Thorez, 1975; Moore & Reynolds, 1997). Fe-smectites occur mainly in the sediments collected in summer, which is in accordance with the generally greater levels of Fe in this mineral group, observed through the intensity ratio $S_{002}/S_{003}$. The ratio between the two species varies according to the reservoirs and in each reservoir, according to the sampling sites, denoting its provenance from distinct parent rocks.

The irreversible collapse after Li-saturation, followed by heating to 300ºC and EG-solvation (Greene-Kelly test, 1955) and the appearance of a sharp, well defined $17.5-17.7$ Å 001 reflection upon glycolation on Mg-saturated samples, indicate the association of montmorillonite and nontronite (Fe-smectite) in the majority of sediments. Montmorillonite is the most common variety although the montmorillonite/nontronite ratio is highly variable throughout the reservoirs. The inference of the Fe content, achieved through the intensity ratio of the 001 and 002 reflections and the frequent absence of the latter at 8.46 Å, indicate a small Fe content in the majority of sediments, denoting again the predominance of montmorillonite over other varieties. Divor smectites have larger Fe levels, as a consequence of the Fe-Mg-rich composition of the source area.

The frequent presence of a broad band at $14-17.5$ Å upon EG solvation followed by a prominent $14-15$ Å tailing reflection with an asymmetry towards 10 Å, discloses the occurrence of interstratification between smectitic and illitic layers, giving medium or poorly crystallized smectites.

*(b) Identification and characterization of chlorite*. Given the mixture of clay mineral groups in the sediments, only the 003 reflection of chlorite (at 4.72 Å) has no superposition on the members of other mineral series. In the sediments having greater amounts of this mineral, the detection of this reflection, often as a weak broadening in the base of $I_{002}$, represented one of the most useful criteria for chlorite identification. The distinction between chlorite and kaolinite was based on the classical
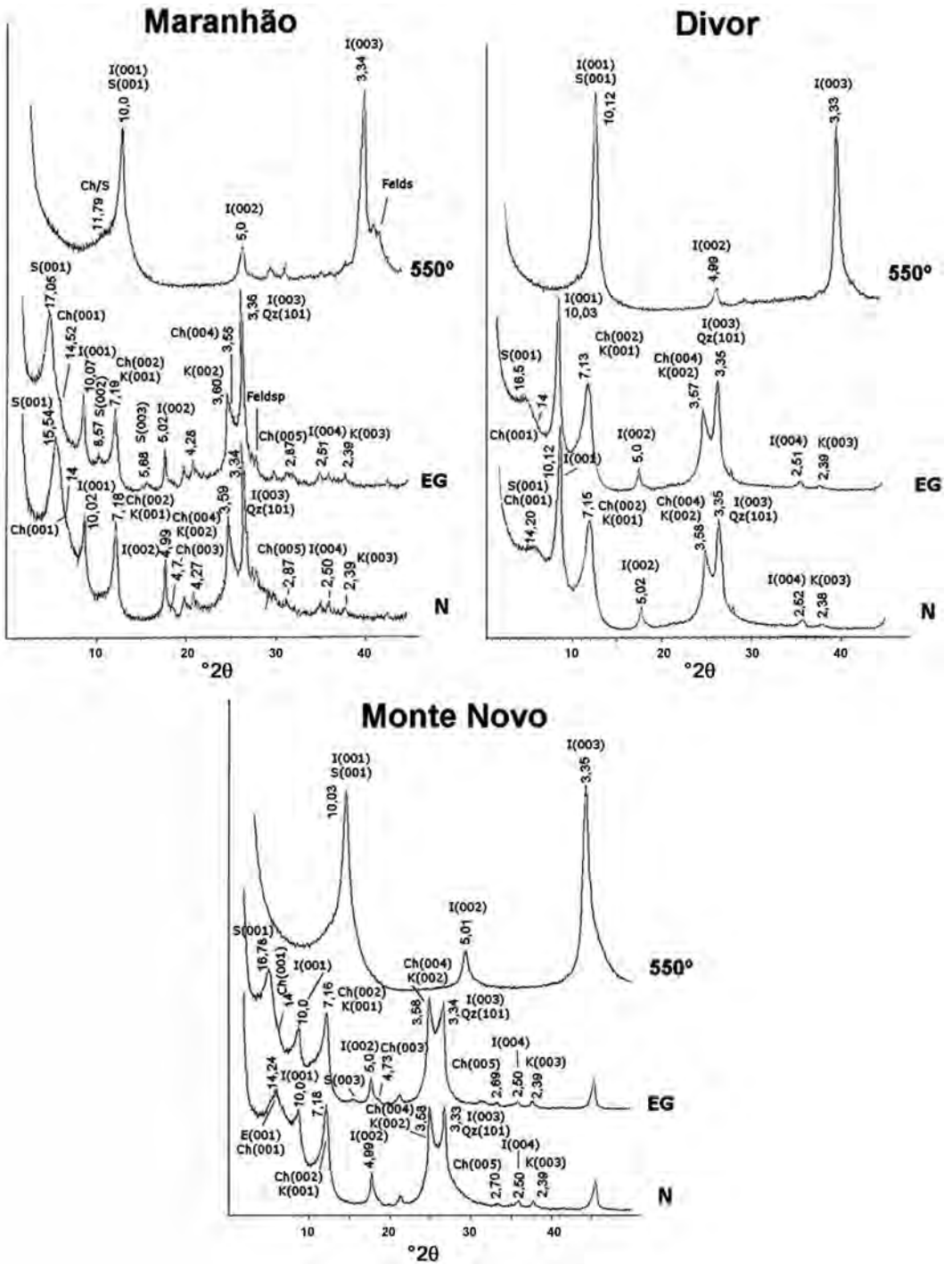
FIG. 3. XRD patterns of some representative samples from Maranhão, Monte Novo and Divor, in the air-dried (N), ethylene glycol-solvated (EG) and heated states (550º).
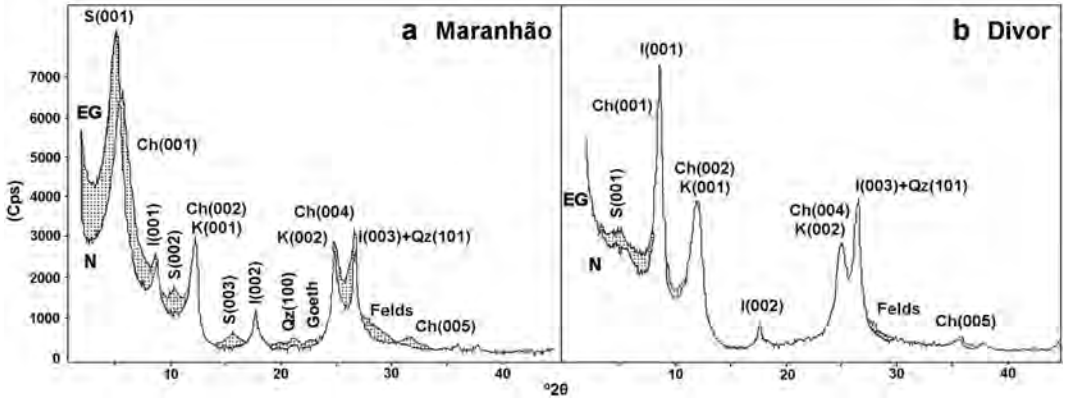
FIG. 4. Comparative analysis of the XRD patterns from two sediment samples with and without the presence of mixed-layered clay minerals. In a sediment from the Maranhão reservoir (a), the asymmetry of illite basal reflections $I_{001}$ and $I_{002}$ towards the low-angle side of the XRD pattern (towards $S_{001}$ and $S_{003}$) and the increase in breadth of the chlorite reflections after glycol solvation, indicate the presence of interstratified expandable layers – I-S and Ch-S. In a sediment from the Divor reservoir (b), after glycolation, the illite and chlorite reflections were not displaced, denoting the absence of mixed-layered structures with smectitic layers.

methods proposed by several authors (e.g. Brattli, 1997; Moore & Reynolds, 1997; Righi *et al.*, 1997): (1) total or partial resolution of the 'doublet' formed by $K_{002}$ and $Ch_{004}$ reflections at 3.56 and 3.53 Å, respectively; (2) identification, when detectable, of reflections which are not interfered with by reflections from other minerals – $Ch_{003}$ at 4.74 Å and $K_{003}$ at 2.38 Å; and/or (3) heating to 550ºC – in chlorite this produces dehydroxylation of the hydroxide sheet with increase in intensity of the 001 reflection and shift from 14 to 13.8 Å and weakening of the reflections of 2nd, 3rd and 4th order. Kaolinite becomes amorphous to X-rays and its diffraction pattern disappears. The distinction between chlorite and smectite and/or vermiculite was achieved under air-dried conditions in K-saturated samples. While chlorite is unaffected by cation saturation, with the 001 reflection remaining at 14 Å, the addition of K collapses smectites and vermiculites to 10 Å.

The occurrence of asymmetrical reflections after heating to 550ºC, EG-solvation and Mg-K-saturation denotes the existence of random mixed layers. In the majority of sediments, it is possible to distinguish two different types: (1) chlorite having small proportions of mixed layers; and (2) chlorite with a high rate of interstratification.

In the Portuguese reservoirs, chlorite abundances correlate with Fe and Mg in the bulk sediments, denoting the Fe-Mg-rich nature of chlorites. Linear correlations between chlorite contents and total

abundances of Fe and Mg are better in Divor sediments (Table 4), in accordance with the structural and chemical characteristics observed in the diffraction patterns. At Divor, Fe shows better correlation values than Mg, reflecting the Fe-rich nature of chlorites.

*(c) Identification and characterization of illite.* In illite, identified by the positions of its 001, 002 and 003 reflections (e.g. Brown & Brindley, 1980; Brattli, 1997; Moore & Reynolds, 1997), the variable 002/001 peak intensity ratio indicates a variable chemical composition of the octahedral sheet, ranging from $Al^{3+}$-rich to $Fe^{3+}$ or $Fe^{3+}$-$Al^{3+}$ dioctahedral illites. Large values for the intensity ratio $I_{001}/I_{002}$ which reflect the preponderance of Fe over Mg, were only observed in the Divor reservoir and in a few sediments of Maranhão, denoting sources richer in Fe. To outline the illite evolution along the reservoirs, the position and breadth of the 001 peak have been determined. This parameter, which represents the symmetry or asymmetry of the reflection and therefore the amount of fixed-K in the interlayer space, can be considered as a measure of illite crystallinity (Brattli, 1997; Moore & Reynolds, 1997).

In relation to crystallinity there are two groups of illites as follows: (1) illites with sharp, narrow and symmetrical reflections, indicating that these minerals could be directly inherited from surrounding soils without any significant degradation or transformation (by stripping the interlayer
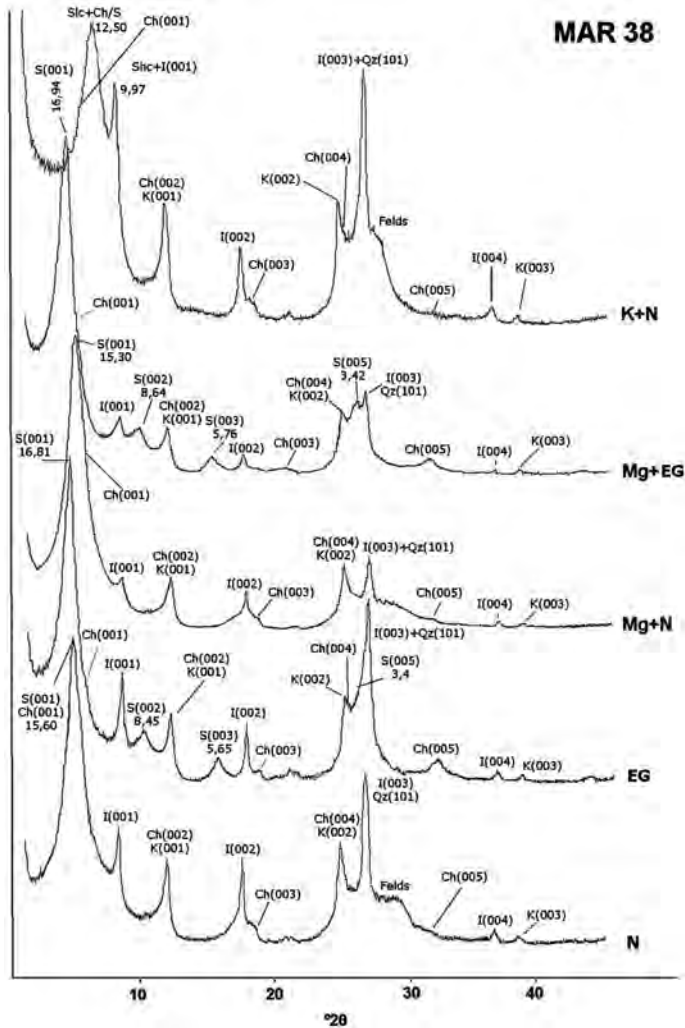
FIG. 5. XRD patterns of one representative sample of Maranhão reservoir, under distinct selective chemical treatments. This figure focuses the criteria used in all the samples for the identification of smectites. Shc − high-charge smectites and Slc − low-charge smectites, N − air-dried, EG − glycol solvation, Mg+N − Mg-saturation in air-dried conditions; Mg+EG − Mg-saturation followed by glycolation, 500º − heating at 500ºC, K+N − K-saturation in air-dried conditions.

$K^+$) during the weathering processes. It is also possible that illite, once deposited in the bottom of the reservoirs, could order its structure by adsorbing and fixing the K dissolved in the water column. (2) Illites with irregular or asymmetrical basal reflections, indicating the 'open character of the illite' due to stripping of the original $K^+$; the displacement of interlayers from 10 to 14 Å upon glycolation characterizes a medium to low degree of crystallinity. These minerals are mainly illites, partly interstratified with variable amounts of expandable layers. Most mixed layers built on illite are of a smectitic nature giving illite-smectite, although smaller amounts of interstratification with chlorite (I-Ch) are observed in a few samples from the Divor reservoir.

*(d) Identification and characterization of kaolinite (kaolin-group) minerals.* After screening of the chlorite reflections often superposed on the kaolinite patterns, by the methods referred to above, kaolin-group minerals were identified from the unchanged 7.1 Å reflection upon glycolation

TABLE 4. Linear correlation values between chlorite contents and total abundances of Fe and Mg in the sediments of Portuguese reservoirs ($r$ – correlation coefficient of Pearson, $r^2$ – determination coefficient and $p$ – significance level). Significance values to $p$ <0.05. $p$ = n.s. (significance values >0.05).

| | | Matrix of linear correlation: chlorite - $Fe_2O_3$; MgO | | | | | |
|---|---|---|---|---|---|---|---|
| | | Maranhão September | Maranhão February | Monte Novo September | Monte Novo February | Divor September | Divor February |
| $Fe_2O_3$ | $r$ | 0.744 | 0.522 | 0.944 | 0.757 | 0.791 | 0.793 |
| | $r^2$ | 0.553 | 0.273 | 0.891 | 0.573 | 0.625 | 0.628 |
| | $p$ | <0.001 | <0.05 | <0.001 | <0.05 | <0.05 | <0.05 |
| MgO | $r$ | 0.401 | 0.394 | 0.634 | 0.545 | 0.474 | 0.591 |
| | $r^2$ | 0.161 | 0.154 | 0.402 | 0.297 | 0.224 | 0.349 |
| | $p$ | n.s. | n.s. | <0.05 | n.s. | n.s. | n.s. |

and from their amorphous behaviour after heating to 550ºC. The intensity of the 00l reflection and its asymmetry both decrease with the degree of disorder (Thorez, 1976). Thus, from the height above background and the position, shape and breadth of the superposed $K_{001}$ and $K_{002}$ reflections and the individual $K_{003}$, it was possible to determine the structural order-disorder of this mineral group. Based on these general principles, three discrete species have been identified: (1) well crystallized kaolinite; (2) medium crystallized kaolinite and (3) disordered kaolinite.

*(e) Identification and characterization of mixed-layer clay minerals*. In most sediments of the Portuguese systems, some of the more common minerals show asymmetry in the air-dried patterns towards low angles and/or produce a large, broad reflection between 10 and 14 Å. This behaviour, according to the methods proposed by Thorez (1976) and Moore & Reynolds (1997), enabled the distinction of three mixed-layered structures often associated with discrete mineral phases: illite-smectite (I-S), chlorite-smectite (Ch-S) and illite-chlorite (I-Ch). (1) I-S: On the basis of peak-position data, we have estimated that the most common transitional phases are mixtures of two types of I-S, one with near 90% illite and the other near 50–60% illite. Among the studied reservoirs, Maranhão shows the most abundant, diverse and widespread mixed-layer clay minerals, especially in the rainy season (winter) with greater hydrodynamic activity and sedimentation rates. In Divor, these minerals are scarce. (2) Chlorite-smectite (Ch-S) does not exceed 10% smectitic layers in Monte Novo and Divor, whereas in Maranhão the smectitic layers amount to 20–40%. (3) Maranhão and Monte Novo sediments almost always contain small amounts of a third type of mixed-layer clay, illite-chlorite, with ~0.5I-0.5Ch.

The mineralogical composition of sediments is quite similar in the three reservoirs and, except for vermiculite, all clay mineral groups are represented, with variation of relative abundances only, reflecting the significant geological variation of drainage basins. In each system, one can observe local and seasonal fluctuation of each mineral group due to the distribution of different sources in the setting area and the hydraulic flow that produces distinct energetic conditions inside the lakes. Clay mineral abundances in the Portuguese reservoirs (Table 5), based on the estimation of integrated intensity of reflections (details above), were calculated using peaks that are very close with respect to 2θ: illite and smectite percentages have been calculated directly from the areas of the glycolated 10 Å and 17 Å peaks, respectively. Given the superposition of reflections of chlorite and kaolinite, the peak areas of both minerals were calculated together in the $Ch_{004}$ and $K_{002}$ reflections at 3.58 Å and 3.54 Å, after deducting the area related to chlorite, and integrating from $Ch_{001}$ at 14 Å (K-saturated + air-dried conditions) or from $Ch_{003}$ at 4.7 Å (glycol solvation conditions). In samples with greater kaolinite contents, the peak area of this mineral in the superposed $Ch_{004}$+ $K_{002}$ was also deduced from $K_{003}$ at 2.39 Å, after application of the intensity calibration factors.

The mineralogical variations of sediments in these reservoirs allow the distinction of sub-areas only differentiated by the relative abundances of the diverse clay mineral groups (Fig. 6).

According to Table 5 and Fig. 6, one can see that the major clay components of the sediments are illite, followed by smectite in Maranhão and by chlorite in the other systems.

TABLE 5. Maximum, minimum and mean values and standard deviation of the relative percentages of clay minerals in the sediments from all sampling periods performed in the Portuguese reservoirs.

| Reservoirs/clay minerals | | | Illite (%) | Smectite (%) | Chlorite (%) | Kaolinite (%) | Vermiculite (%) |
|---|---|---|---|---|---|---|---|
| Maranhão | | | | | | | |
| | September | Mean V. | 39.0 | 31.4 | 16.6 | 13.0 | – |
| | | Maximum V. | 53.9 | 46.0 | 27.3 | 22.9 | – |
| | | Minimum V. | 24.2 | 13.6 | 5.9 | 3.9 | – |
| | | Stand. deviation | 8.44 | 8.74 | 5.90 | 4.83 | – |
| | February | Mean V. | 44.6 | 28.9 | 10.6 | 15.1 | Vest. |
| | | Maximum V. | 63.0 | 50.2 | 15.8 | 27.6 | Vest. |
| | | Minimum V. | 28.8 | 15.2 | 4.5 | 3.3 | Vest. |
| | | Stand. deviation | 7.97 | 8.44 | 3.53 | 7.01 | |
| Monte Novo | | | | | | | |
| | September | Mean V. | 38.7 | 10.5 | 27.6 | 23.2 | – |
| | | Maximum V. | 50.0 | 16.5 | 36.0 | 35.0 | – |
| | | Minimum V. | 24.3 | 5.8 | 23.0 | 13.5 | – |
| | | Stand. deviation | 7.93 | 3.06 | 3.80 | 6.61 | – |
| | February | Mean V. | 31.1 | 15.6 | 26.6 | 26.8 | – |
| | | Maximum V. | 44.0 | 30.2 | 36.8 | 34.1 | – |
| | | Minimum V. | 21.4 | 8.0 | 19.2 | 15.9 | – |
| | | Stand. deviation | 6.79 | 6.28 | 5.00 | 5.72 | – |
| Divor | | | | | | | |
| | September | Mean V. | 60.9 | 4.4 | 18.8 | 15.9 | – |
| | | Maximum V. | 73.3 | 14.1 | 24.9 | 25.9 | – |
| | | Minimum V. | 50.5 | 0.0 | 15.8 | 8.1 | – |
| | | Stand. deviation | 8.30 | 4.14 | 3.24 | 5.80 | – |
| | February | Mean V. | 65.4 | 5.1 | 16.9 | 12.6 | – |
| | | Maximum V. | 73.0 | 7.5 | 22.4 | 20.6 | – |
| | | Minimum V. | 58.5 | 1.2 | 11.3 | 7.2 | – |
| | | Stand. deviation | 4.87 | 1.93 | 3.53 | 4.17 | – |

(i) Smectite abundances decrease progressively in the following order: Maranhão → Monte Novo → Divor. In Maranhão and Divor, the increase in smectite in September correlates with the annual period of greater settlement of most fine-grained particles, when the hydrodynamics are less intense. In Monte Novo the sedimentation of the fine-size fraction takes place predominantly in the period of higher leaching rates (February) in which smectite shows a significant increase. In both cases smectite is concentrated in the finer-grained fractions of sediments.

(ii) Chlorite and kaolinite are more abundant in Monte Novo, showing similar proportions throughout the annual cycle. The summation of both minerals is similar in Maranhão and Divor, though kaolinite predominates in the former and chlorite in the latter reservoir. In all three systems, chlorite often shows interstratifications with expan-

sive layers, producing a mixed-layered structure like chlorite-smectite.

(c) In the Divor reservoir, illite dominates and shows less variety and a smaller proportion of interstratified layers, while in Monte Novo, values do not exceed 40%. In Maranhão, which represents an intermediate situation, as in Divor, illite becomes more abundant in rainy February.

(d) Vermiculite appears in small amounts in a few sediments of the Maranhão reservoir only, seldom exceeding 3%.

## (2) Clay minerals in the Brazilian reservoir

The positions of the reflections under natural, air-dried, glycolated and heated conditions define a set of clay minerals less diverse than in the Portuguese reservoirs, dominated by kaolinite (near 80% on average) and Fe/Al oxides, followed by lesser
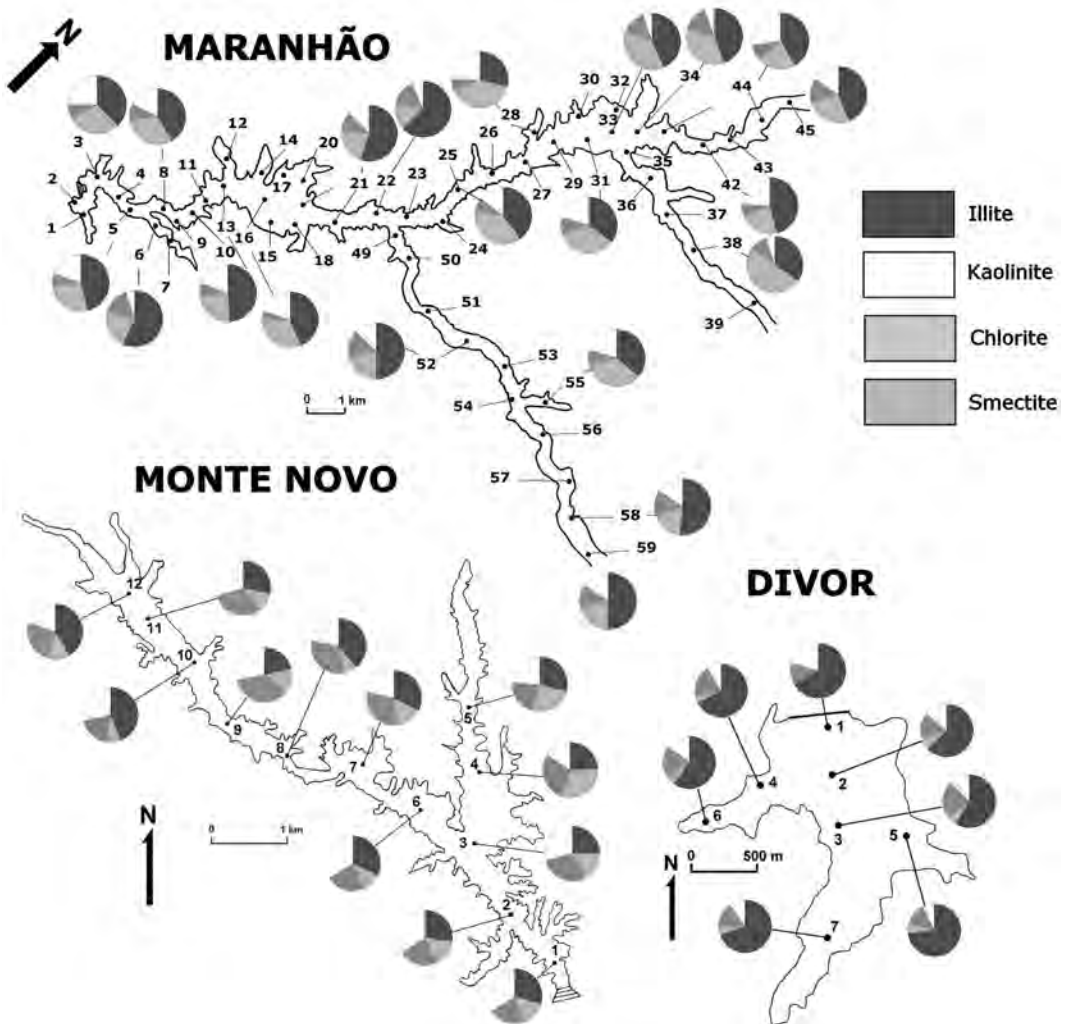
FIG. 6. Distribution of the clay mineral groups in the clayey fraction of sediments of Maranhão, Monte Novo and Divor reservoirs. All the values correspond to winter conditions in February.

amounts of chlorite, and a uniform distribution of abundances and chemical/structural characteristics of minerals along the reservoir (Fig. 7). The asymmetry, low-intensity, enlarged-foot and broad reflections in XRD patterns denote the occurrence of clay minerals with a medium−low degree of crystallinity.

The clay minerals of the Brazilian reservoir exhibit a greater degree of structural disorder than those of the Portuguese reservoirs, denoted by more asymmetrical, weakened and broadened reflections at the low- and high-angle sides of XRD patterns.

The 10 Å and 5 Å reflections are absent, which means that illite is not present. The presence of a small but well defined peak at 14−15 Å in air-dried samples followed by the absence of (i) a 17−18 Å peak in ethylene glycol-solvated preparations and (ii) a 10 Å peak after heating to 550ºC, indicate the presence of chlorite and the absence of expandable minerals like smectites (Fig. 8). Kaolinite was identified through the position of the 002, 003 and 004 basal reflections, beyond the position of the most intense first-order peak, nearly superposed on the chlorite 002 peak.
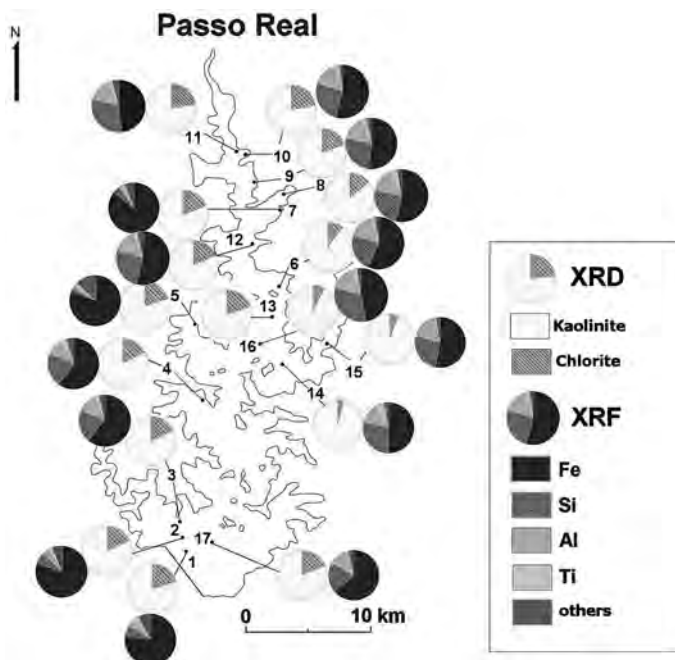
FIG. 7. Distribution of clay minerals and major elements (X-ray fluorescence) in the clayey fraction of Passo Real sediments.

## DISCUSSION

### *Weathering mineralogy of rocks and soils from the drainage areas*

In the drainage areas of the Portuguese reservoirs, the wide variety of minerals formed throughout the various alteration stages, from unaltered rock to soil formation, reflects a large number of mineralogical transformations throughout the weathering process. Transport and deposition in reservoirs will further contribute to a large diversity of clay minerals in the sediments accumulated in these systems.

In contrast, large amounts of rainfall with a regular distribution over the year, typical of the sub-tropical climate which characterizes the Brazilian system, increase the kinetics of chemical reactions and favour biological activity and transformation of organic matter, determining strong and uniform weathering processes. These stronger and faster alteration mechanisms (when compared with those in the Portuguese examples) over a far more homogeneous lithology, mainly basaltic, generate a small diversity of clay minerals in the weathered rocks. Primary minerals are decomposed at the early stages of alteration

(Schenato *et al.*, 1995) giving clay minerals characteristic of the intermediate–final stages of weathering, with intense leaching of divalent cations and low concentrations of silica.

### *Significance of the clay minerals in sediments of both groups of reservoirs*

The large variety and the complex clay mineral assemblages in the sediments of the Portuguese reservoirs is favoured by the Mediterranean climate of southern Portugal associated with (1) remarkable variation of the drained lithologies, (2) weak intensity of rock weathering (3) various alteration states of weathering products, and (4) mixture after transport and sedimentation mechanisms. The various clay fractions contain the same mineral species, only with some variation of the relative abundances and some structural and chemical aspects, denoting inheritance from distinct parent rocks or the existence of diverse physical and chemical conditions in the deposition environment. In contrast, at Passo Real the sub-tropical climate typical of southern Brazil enhances (1) high-intensity rock weathering, (2) leaching of soluble elements (Ca, Na, K, Mg) and preferential
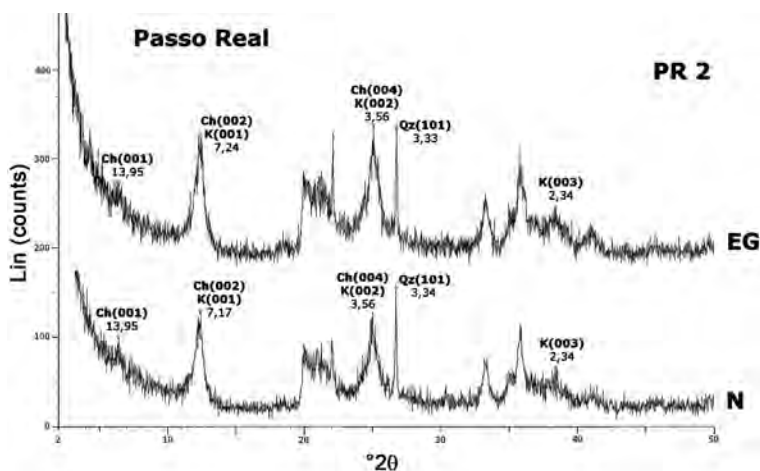
Fig. 8. XRD pattern of a sample from the Passo Real reservoir under natural air-dried and ethylene glycol-solvated conditions.

accumulation of stable elements (Si, Al, Fe), and (3) intense transformation processes during cycles of erosion-transport-accumulation in the bottom of the flood basin. These mechanisms, coupled with an homogeneous basaltic composition of parent rocks, produce a smaller variety of minerals characterized by simpler clay assemblages.

According to Velde (1995), mixed-layer clay minerals seem to be an expression of change in the mineral stability, one phase becoming stable at the expense of another. Thus, an environment characterized by continuous chemical modifications, such as a dam reservoir, is appropriate to the formation of mixed-layer clays, which easily explains the great variety of mixed-layered structures identified in the sediments. Though Fe oxides and hydroxides are not clay minerals, they are usually abundant in the clay-size fraction, having an important role in the sediments of Passo Real. Their significant presence in the bottom of this Brazilian reservoir indicates that these sediments have, as their main source, the extreme leaching of soils from the drainage area and rarely materials developed from the early stages of rock weathering.

## Mineralogical transformations from soils to reservoirs

The comparative study between the weathering mineralogy of rocks and soils of the drainage basins and the clay mineralogy of the reservoir sediments indicates that, from the erosion of basins upstream

to the deposition in the reservoirs, the clay-size weathered particles, mainly composed of clay minerals, have been affected by complex transformations of both chemical and physical nature. These transformations produce a simpler clay assemblage, denoting a higher mineralogical evolution and may occur in two steps: (1) during transport and transitory deposition in river streams; and (2) after its final deposition within the reservoirs.

### (1) Mineralogical transformations in Portuguese reservoirs

*(a) Absent or scarce vermiculite.* Vermiculite has been identified by Abreu (1986), Vieira e Silva (1990) and Fonseca (2000) in significant amounts in soils of the drainage basins of the studied reservoirs. The absence or near absence of this mineral in the reservoir sediments is probably a consequence of the classic transformation sequence leading to the acquisition of expandable layers (*i*: trioctahedral vermiculite → trioctahedral smectite; and *ii*: dioctahedral vermiculite → dioctahedral smectite, e.g. Grim, 1968). This can occur either in the parent soils or during the complex cycles of transport and deposition within the reservoirs, and could also explain the high levels of smectite found in the sediments of the Maranhão and Monte Novo systems.

*(b) Larger illite contents.* The larger illite contents in sediments, with respect to its concentration in the weathering products of parent soils and

rocks, suggest the occurrence of aggradative transformations involving fixation mechanisms of $K^+$ within the structure of some clay minerals (kaolinite, smectite). The enrichment of K in the environment, according to Wilson (1999), is often a consequence of excessive fertilization in agricultural areas. These processes (Hillier, 1995; Wilson, 1999) can be resumed through schematic reactions as follows: (1) kaolinite $+ K^+ \rightarrow$ illite; and (2) smectite $+ K^+ \rightarrow$ illite $+$ released cations ($Ca^{2+}$, $Mg^{2+}$, $Fe^{3+}$, $Na^+$).

*(c) Greater contents of mixed-layered structures.* In an alteration environment such as a soil or the leaching and deposition of particles inside aqueous basins, the most common mineralogical transformation processes have a few steps which lead to synthesis of intermediate phases, usually mixed-layer clay minerals (Hillier *et al.*, 1996; Ko *et al.*, 1998; Meunier *et al.*, 1998). This can easily explain the profuse presence of these minerals in the reservoir sediments. Interstratified minerals can be inherited directly from the parent weathered rocks or soils overlying them (Righi & Meunier, 1995; Ko *et al.*, 1998; Moore & Reynolds, 1997; Meunier *et al.*, 1998; Wilson, 1999). However, they can also be formed during the cycles of erosion-transport-accumulation, explaining their greater levels. Illite-smectite, the most abundant interstratified mineral of the overall sediments as well as of the weathering products of the source areas (Fonseca, 2000), can result from the conversion of illite to smectite which, according to some authors (Buey *et al.*, 1998; Ko *et al.*, 1998; Meunier *et al.*, 1998), has a greater chance in this kind of environment than the reverse (smectite $+ K^+ \rightarrow$ illite). The illite-smectite conversion involves release of interlayer $K^+$, decrease of $Al^{3+}$ and increase in $Si^{4+}$ and $Mg^{2+}$. After these gain and loss reactions, the surface charge decreases: illite $- K^+ + (Si^{4+}, Mg^{2+}) \rightarrow$ vermiculite $\rightarrow$ smectite.

*(d) Greater structural order.* In the XRD patterns of sediments, clay mineral reflections are generally more defined, regular and symmetrical than those of the corresponding minerals in the weathered products of the source areas (see Fig. 9). These structural differences indicate an increase in the degree of order of some mineralogical groups, from its original synthesis in soils to its accumulation inside the reservoirs. Thus, though most of the clay minerals in the sediments are inherited directly from the parent rocks and soils, during the erosion-transport-deposition cycle, they could encompass

significant aggradative transformation mechanisms, like the incorporation and reordering of cations existing in the soluble phase within the structure of previously depleted minerals.

## (2) Mineralogical transformations in the Brazilian reservoir

The sediments of Passo Real have a simpler clay assemblage, which denotes a higher mineralogical evolution, dominated by extreme leaching of soluble elements during soil erosion. This is accelerated by the high intensity of rock weathering in an environment characterized by (1) low pH (4.3 < pH < 5.9), (2) high water/rock ratio, (3) high leaching rates and salt movement (K/Na/Mg/Ca), (4) low activity and partial dissolution of Si, and (5) high accumulation of stable elements Al-Fe (Righi & Meunier, 1995). The main reactions may be as follows: (1) smectite $\rightarrow$ kaolinite-expanding minerals $\rightarrow$ kaolinite $\rightarrow$ gibbsite; (2) illite $\rightarrow$ illite-vermiculite $\rightarrow$ vermiculite $\rightarrow$ vermiculite-smectite $\rightarrow$ smectite $\rightarrow$ kaolinite $\rightarrow$ gibbsite; (3) chlorite $\rightarrow$ chlorite-vermiculite $\rightarrow$ vermiculite $\rightarrow$ vermiculite-smectite $\rightarrow$ smectite $\rightarrow$ kaolinite $\rightarrow$ gibbsite.

If weathering and leaching conditions are very intense, a few intermediate phases will not form (Wilson, 1999). This means that during the erosion and transport of particles from soils to the reservoir, illite (the major weathering mineral from the acid volcanic rocks and the detrital formation of Tupanciretã) can be directly transformed into kaolinite, without intervening vermiculization. In
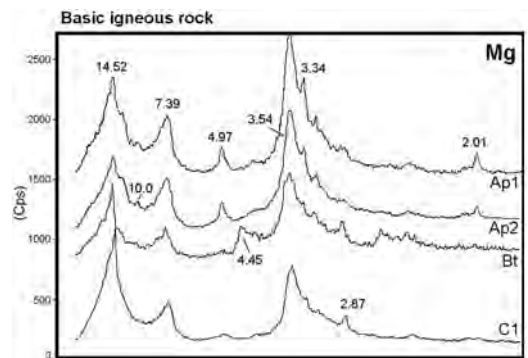


FIG. 9. XRD patterns (upon Mg saturation) of the clayey fraction of a soil derived from basic igneous rocks in the drainage area of the studied reservoirs (from Fonseca, 2000, reproduced with permission). The figures denote *d* spacings.

this kind of transformation, which leads to the synthesis of secondary kaolinite (according to Murray, 1999), there occurs a prompt $K^+$ leaching associated with some Si displacement and the incorporation of Fe as an isomorphic substitute (Murray, 1999; Wilson, 1999).

## CONCLUSIONS

Because of the critical state of the global soil problem, we investigated the possibility of removing dam reservoir sediments and returning them to the soils of the drainage areas from whence they came (Fonseca, 2002; Fonseca *et al.*, 1993, 1998, 2003). A key aspect is the effect of the mineralogical transformations of clay minerals from over-eroded soils to the bottom of dam reservoirs. We conclude that clay minerals are much more active and nutrient-rich in the reservoir environment than in parent soils. Two groups of studied reservoirs, in Portugal and Brazil, show mineralogically distinct clay fractions. Diverse factors determine the mineralogy of sedimentation, namely: (1) climatic conditions (temperate *vs.* sub-tropical) and (2) parent-rock composition.

In the Portuguese reservoirs, the Mediterranean climate of southern Portugal and the large rock diversity in drainage basins associated with (1) various alteration states of weathering products, (2) mixture after transport and sedimentation mechanisms, and (3) variation of the flocculation rates of the distinct clay groups, result in a large variety of clay minerals and, in each system, to a significant spatial and temporal mineralogical, structural and chemical diversity. The nature of the clay minerals reflects the lithology of parent rocks, a common situation in areas characterized by weak rock weathering, not enough to obliterate the main composition of source materials.

Comparative mineralogical study of the weathered source rocks and the reservoir sediments demonstrates the effect of aggradative transformation processes, which may explain the major differences encountered: (1) decrease or absence of vermiculite, (2) increase of illite, (3) large occurrence of mixed-layered structures; and (4) increase in the structural order of some groups. These processes, involving cation exchange and fixation mechanisms, may occur during the complex cycles of transport and deposition of inherited clays, including variable alteration sequences such as: (1) evolution of vermiculites

into smectites; (2) kaolinite and smectite illitization; (3) transformation of micaceous minerals into vermiculite and smectite; and (4) smectite chloritization or the reverse-sense reaction.

The more homogeneous composition of the parent rocks for the Brazilian reservoir discloses (1) the lesser diversity of the clay minerals of sediments dominated by kaolinite and Fe/Al oxides and (2) a uniform distribution of abundances and chemical/structural characteristics of minerals along the reservoir. Relative to the weathering mineralogy of rocks and soils of the drainage area, sediments have simpler clay assemblages, denoting a more advanced stage of evolution, characteristic of a subtropical climate, which leads to a much greater intensity of rock and soil weathering followed by extreme leaching of soluble elements.

The ultimate goal of our studies is using reservoir sediments in agriculture to help solve the growing problem of world desertification. Given the mineralogical transformations of clay particles from over-eroded soils to their retention in artificial lakes, the mineralogy of the clay fraction of sediments is markedly more advantageous than that of the parent soils in the drainage basins This situation, much more evident in the Portuguese systems, is due to the large variety of minerals present, including expanding clay minerals, often randomly interstratified and medium crystallized or disordered; these mineralogical characteristics enhance high cationic adsorption and exchange capacity and the use of nutrients by plants, through slow release of components from relatively loose crystal structures. Beyond the quality of dam sediments for agricultural purposes, if used as soils or fertilizers, their extraction could also greatly benefit reservoir waters, through reduction of excessive amounts of components such as organic matter and phosphates.

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