

conditions. However, Irion and Zolmer (1990) concluded that fifteen percent of the solid load drained to the oceans by rivers consists of silty and clayey sediments, representing about half of total marine sediments. Thus, even if silt and clay occur as traces (less than 1%) it is very important to look to both fractions, specifically to the clay minerals. The study area of the present study is located between Espinho and Cape Mondego, in the Portuguese western coast, and our main goal is to identify the clay minerals distribution patterns in the recent dune littoral deposits, after having been remobilized from the neighbouring beach deposits.

The clay mineral suites identified in the beach and dune deposits are similar, consisting of illite, kaolinite, illite/smectite random mixed-layers, chlorite, kaolinite/smectite random mixed layers, illite/chlorite random mixed layers and smectite.

The more abundant clay minerals (in contents higher than 10%) are illite, illite/smectite random mixed-layers and kaolinite. Chlorite and kaolinite/smectite mixed layers exhibit contents lower than 10%, whereas illite/chlorite mixed-layers and smectite appear as traces (lower than 2%).

Kaolinite, illite/smectite random mixed-layers and chlorite exhibit different contents, either in the beach deposits or in the dune deposits. Kaolinite content of the dune deposits is significantly higher than in the beach deposits, whereas illite/smectite random mixed-layers content is significantly lower in the dune than in the beach deposits.

Illite's Esquevin indexes don't show significant differences for both deposits, pointing out to similar crystallochemical characteristics of the illites found in the beach and in dune deposits. However, Kubler index values corresponding to the same illites suggest distinct crystallinities. In fact, illites from the dune deposits show higher Kubler index values than those showed by illites from beach deposits, indicating that illites from the dune deposits are more degraded than those from the beach deposits.

In conclusion, the results obtained in the

present study point out to the occurrence of more pronounced clay minerals degradation in the dune deposits, probably related to the effect of incipient pedogenetic processes.

### **Pedogenic Clay Minerals from a Brown-Black Soil Sequence on Basalt in Sardinia**

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Clay minerals from soils of a brown-black soil sequence developed from basaltic parent material in Sardinia were characterized. Soils are located along a short toposequence (200 m) with only a very small change of elevation (1 m). In the lower part of the sequence, soil is a clay-rich black Vertisol, whereas at the upper part soil is a brown Inceptisol. Clay content is more than 600 g kg<sup>-1</sup> for all horizons in the Vertisol and about 400 g kg<sup>-1</sup> in the brown Inceptisol.

The clay fraction was extracted by centrifugation and freeze-dried. Characterization includes X-ray diffraction, infra-red spectroscopy (FTIR), cation exchange capacity and permanent and variable charges analysis. X-ray diffraction data showed contrasting clay mineralogy according to soil horizon and topographic position of the soil. Clay minerals in the brown Inceptisol are dominated by kaolinite-smectite mixed layers whereas the Vertisol contains mainly smectite and kaolinite-smectite mixed layers with a small proportion of kaolinite. No important mineralogical changes were observed according to soil horizon in the brown Inceptisol, except that IR spectroscopy indicates a strong decrease of "crystallinity" for the clay minerals from the C to the Ap horizon. In the Vertisol, the proportion of

kaolinite layers in the kaolinite-smectite mixed layers increases from the C to the Ap horizon. This soil clay-mineral distribution, in relation to topography, is similar to that reported for (kaolinitic) red-black (smectitic) soil association in subtropical areas. Drainage conditions induced by the slope gradient are thought to govern the soil clay mineralogical evolution. The slope promotes downward movement of water, which removes silica and soluble cations (which favor the formation of kaolinite). Concentration of soil solutions induced by evaporation in the lower part of the sequence favor the formation of smectites. However, increasing proportion of kaolinite in the top horizons of the Vertisol could be attributed to particle transport from the upper part of the sequence by runoff events. Soil surface-properties are related to clay mineralogy. Especially, more than 50% of the CEC is due to pH-dependent charges in the brown Inceptisol, but derives, up to about 75%, from accessible permanent charges in the Vertisol.

### **Adsorption of Heavy Metals on Fe-Al Oxides as Affected by pH and Low Molecular Mass Organic Ligands**

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In soil environments, particularly in the rhizosphere soil, chelating organic ligands (or oxalate and tartrate), have an important role in the mobilization of heavy metals. Heavy metals are specifically adsorbed on variable charge minerals and soils forming inner-sphere complexes. Organic anions may influence heavy metal adsorption by modifying the surface properties of minerals on which they

are adsorbed and by forming Me-Lx complexes of different nature and affinity for the surfaces of soil.

We studied: 1) the adsorption of Cu, Co, Pb and Zn at pH 3.0-8.0 on Fe-Al oxides formed at initial Fe/Al molar ratios of 0, 1, 2, 4, 10 and ∞; 2) the competitive adsorption between Cu and Zn on a metal oxide; and 3) the influence of different concentrations of oxalate or tartrate on the adsorption of Pb at pH 4 on the mixed Fe-Al gels.

Mixed Fe-Al oxides were prepared by precipitating mixtures of Fe and Al ions at initial Fe/Al molar ratios (R) of 0, 1, 2, 4, 10 and ∞ (R0, R1, R2, R4, R10 and R∞).

The heavy metals were selectively adsorbed on the oxides. The selectivity sequence was Pb<sup>2+</sup> > Cu<sup>2+</sup> > Zn<sup>2+</sup> > Co<sup>2+</sup>, but the pH at which 50% of each cation was adsorbed (pH<sub>50</sub>) was different from sample to sample. It was found that usually the greater the amounts of Fe in Fe-Al gels the lower the pH<sub>50</sub> for each metal, but the adsorption of a heavy metal was not linearly related to Fe content.

Competitive adsorption of Cu and Zn on ferrihydrite (R∞) showed that Cu strongly prevented Zn adsorption even at an initial Zn/Cu molar ratio of 8, whereas Cu sorption was not inhibited.

In the presence of oxalate (OX) or tartrate (TR) [organic ligand/Pb molar ratio (r<sub>i</sub>) from 0 to 7] the quantities of Pb adsorbed on the Fe-Al oxides usually increased with increasing r<sub>i</sub>. The adsorption of Pb on the oxides has been influenced not only by the presence and concentration of organic ligands but also by the sequence of addition of Pb and tartrate on the sorbents.

### **Green Rust – A Precursor For Iron(hydr)oxides**

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