

Geochemical proxies for changes in dust sources in Negev desert loess

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The loess of the Negev desert of Israel, was deposited mainly during the late Pleistocene [1, 2]. It is characterized by a bimodal grain-size distribution with modes between 2-8 micrometer (fine silt) and 50-60 micrometer (coarse silt) that represent two different sources of dust, one distal and one proximal [3].

Here we investigate the carbonate-free samples of the two size fractions and search for a geochemical signature of the distal and proximal sources of the loess in three OSL-dated primary loess sequences along a climatic transect: Hura village (~250 mm/yr) and Ramat Beka (~150 mm/yr) in the northern Negev and Mt. Harif (~100 mm/yr) in the central Negev. The fractions are separated and analyzed for major and trace elements and for Sr and Nd isotopic composition. Preliminary results show differences between the fine and coarse fractions that agree with the observation of two different sources contributing to loess in the Negev. Sr-Nd isotopic ratios of both silt fractions suggest contribution from several distal (e.g. Sahara, Arabia) and local proximal sources (e.g. Sinai deserts, Nile delta sediments, and the Sinai-Negev sand dunes). Moreover, changes in loess sources over time were detected in shifts in Sr and Nd isotopic values of the fine fractions, these shifts occur at ~60-70 kyr in Mt. Harif and Ramat Beka sites and at ~20 kyr at Hura site.

These results support the formation model of primary desert loess by eolian abrasion of sand dunes and suggest that the loess chemical and isotopic composition reflect changes of dust sources over time.

[1] Crouvi *et al.* (2009) *Journal of Geophysical Research* **114** (F02017), 1-16.

[2] Amit *et al.* (2011) *Geological Society of America Bulletin* **123**, 873-889.

[3] Yaalon and Dan (1974), *Zeitschrift für Geomorphologie Supplementband* **20**, 91-105.

CHARACTERIZATION OF HUMIC ACID REACTIVITY MODIFICATIONS DUE TO ADSORPTION ONTO α - Al_2O_3

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Adsorption of purified Aldrich humic acid (PAHA) onto α - Al_2O_3 is studied by batch experiments at different pH, ionic strength and coverage ratios R (mg of PAHA by m^2 of mineral surface). After equilibration, samples are centrifuged and the concentration of PAHA in the supernatants is measured. The amount of adsorbed PAHA per m^2 of mineral surface is decreasing with increasing pH. At constant pH value, the amount of adsorbed PAHA increases with initial PAHA concentration until a constant pH-dependant value is reached.

UV/Visible specific parameters such as specific absorbance SUVA_{254} , ratio of absorbance values E_2/E_3 and width of the electron-transfer absorbance band Δ_{ET} are calculated for supernatant PAHA fractions of adsorption experiments at pH 6.8, to have an insight on the evolution of PAHA characteristics with varying coverage ratio. No modification is observed compared to original compound for $R \geq 20 \text{ mg}_{\text{PAHA}}/\text{g}$. Below this ratio, aromaticity decreases with initial PAHA concentration. Size-exclusion chromatography - organic carbon detection measurements on these supernatants also show a preferential adsorption of more aromatic and higher size fractions.

Spectrophotometric titrations were done to estimate changes of reactivity of supernatants from adsorption experiments made at $\text{pH} \approx 6.8$ and different PAHA concentrations. Evolutions of UV/Visible spectra with varying pH were treated to obtain titration curves that are interpreted within the NICA-Donnan framework. Protonation parameters of non-sorbed PAHA fractions are compared to those obtained for the PAHA before contact with the oxide. The amount of low-affinity type of sites and the value of their median affinity constant decrease after adsorption. From PAHA concentration in the supernatant and mass balance calculations, "titration curves" are obtained and fitted for the adsorbed fractions for the first time. These changes in reactivity to our opinion could explain the difficulty to model the behavior of ternary systems composed of pollutants/HS/mineral since additivity is not respected.

Figure 1: LC-OCD chromatograms of PAHA and of supernatants from adsorption experiments at 0.1M and $\text{pH} \approx 6.8$ (R in $\text{mg}_{\text{PAHA}}/\text{g}$ α - Al_2O_3).

