Buried lava paleosol in NW Fogo island (Cape Verde) – chemical and mineralogical evolution

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In Fogo island (Cape Verde archipelago), buried paleosoils developed between alkaline lava flows occur. Six samples (from parent rock to paleosurface) were collected from a 1 m thick profile. Weathered samples vary in colour from dark brown to yellowish. Chemical and mineralogical analyses were performed by instrumental neutron activation analysis, Mössbauer spectroscopy and X-ray diffraction.

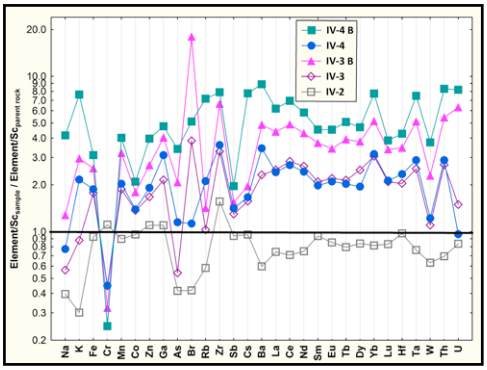

Fig. 1 – Chemical variations with depth/weathering degree (after normalization to Sc)

The main minerals of the parent rock identified by XRD are pyroxenes, olivines and phyllosilicates. In the paleosol only pyroxenes, quartz, phyllosilicates and in the most weathered/surficial samples hematite, were clearly identified.

Except for Cr a general enrichment of the studied chemical elements occurs with increasing weathering (Fig.1). The ancient surficial level has a significant enrichment in Na, K, Rb, Cs, Ba, REE, Ta, Th and U. Bromine variations may be mainly related with the presence of fluorapatite detected by XRD. Iron has a conservative behaviour. As the weathering degree increases the Fe^{3+}/Fe^{2+} ratio increases from 35% up to 85% and hematite is formed.

Bottom up approach for the predictive modelling of sorption isotherms on argillaceous rocks

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Sorption in natural argillaceous rocks is inherently too complex and multi-faceted to be mechanistically predicted. The so-called "bottom up" approach for argillaceous rocks is based on the hypothesis that the uptake of sorbates in such complex systems can be quantitatively described based on the understanding of the sorption mechanisms on 2:1 type clay minerals [1]. Illite and illite/smectite mixed layers are the major clay mineral components of many argillaceous rocks, and their properties are supposed to be responsible for the radionuclide uptake in these systems.

The aim of this work is to test the capabilities of the 2SPNE SC/CE sorption model [2] and of the generalised sorption model for Cs [3] to make blind predictions of the sorption isotherms in two argillaceous rocks, Boda Clay Formation (BCF) and Opalinus Clay (OPA). As a complementary tool Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy is used to verify the assumptions made in this approach.

Sorption isotherms of Cs(I), Ni(II), Co(II) and Eu(III) were measured on BCF and OPA rock samples in their respective pore-waters. The sorption prediction on these argillaceous rocks was then carried out using the mechanistic sorption models developed for illite [2, 3], and the results scaled over the illite and illite/smectite weight content in the sample. Generally a good agreement between the measured data and the predicted values was found. However, some discrepancies were observed, e.g. for Ni(II) on BCF at higher Ni(II) equilibrium concentrations. EXAFS was therefore used to verify the sorption mechanisms along the isotherm at the molecular level. In the isotherm region, where prediction and measurement coincide, sorption was in fact the only uptake-controlling mechanism. In contrast, EXAFS showed precipitation as additional uptake processes in the isotherm regions where prediction and measurement deviated.

[1] Bradbury & Baeyens (2000) *Appl. Clay Sci.* **52**, 27-33. [2] Bradbury & Baeyens (2009) *Geochim. Cosmochim. Acta* **73**, 1004-1013. [3] Bradbury & Baeyens (2000) *J. Contam. Hydrol.* **42**, 141–163.

DOI:10.1180/minmag.2013.077.5.13