Short scale changes in soil properties due to structural iron reduction.

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Introduction

Cation exchange capacity (CEC) is one of the most important soil parameter, determining major retention and physical soil properties. CEC is due to cation heterovalent substitutions in the clay crystal and is therefore considered as a constant. As reviewed in Stucki (1997), structural iron (Fe_s) in the clay lattice of pure clay can be reduced, resulting in sharp changes in clay layer charge and CEC. Favre et al. (2002) reported simultaneous structural iron reduction and CEC increase in field and incubated bulk soil. Induced by bacteria, soil reduction may occur on short time and space scale. The redox-induced changes in CEC, exchangeable cations and clay particle organization in a rice-cropped vertisol with 40% of iron-bearing smectite are presented here.

Methods

Eh and pH were monitored in the field and in laboratory incubated bulk soil samples with native bacteria. Soil samples were collected in incubators at different Eh values. Structural iron reduction was assessed using chemical analysis and Mössbauer spectroscopy. Changes in clay texture and organization were observed using TEM images. Experiments were performed under N_2 atmosphere to avoid re-oxidation.

Results and discussion

CEC increased two times upon reduction. The increase was related to structural iron reduction. The CEC increase was almost balanced by Fe^{2+} and NH_4^+ adsorption without release of other cations (see table below). Reductive dissolution of iron oxides was simultaneously observed. TEM images showed sharp changes in clay organisation, namely increase in particle thickness, elongation and stacking order.

E_H	Fe^{II}_s	CEC	Ca_x	Mg_x	Na_x	K_x	Fe^{2+}_x	$NH_4^+{}_x$
[V]	[%]	[$cmol_c^+ kg^{-1}$]						
0.4	0.1	22.6	15.1	10.2	0.5	0.5	0.0	0.2
0.0	0.8	55.0	10.8	6.8	0.1	0.4	18.3	7.1

Conclusions

These results show that structural iron reduction actually occurs in field conditions and changes major soil physical and retention properties. Structural iron and iron oxides seem to be reduced at similar redox potentials. This process is likely to occur either on large or short time and space scales in soils and sediments.

References

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A new method for U-Pb isotopic analyses of uranium oxide minerals by SIMS

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We present a new SIMS method that combines the advantages of conventional U-Pb dating (*i.e.*, use of concordia) and *in situ* analysis, and therefore is ideally suited for the study of chemically complex and fine-grained uranium-oxides associated with uranium deposits. During SIMS analysis, differences in the chemical composition of the target phase can affect both relative ion-yields among the isotopes of a given element, and between different elements (e.g., U^+ and Pb^+). These matrix effects can lead to erroneous elemental and isotopic ratios determinations if not corrected (e.g., Holliger, 1991). Therefore, an ion-yield normalizing coefficient (αSIMS) that accounts for variation in relative ion-yields with chemical composition for the mineral of interest is necessary. We assembled a suite of uraninite standards that cover a range of U and Pb compositions to develop an appropriate empirical mass bias model. The $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ratios measured for each standard by TIMS were compared to the $^{206}Pb^+/^{238}U^+$ and $^{207}Pb^+/^{235}U^+$ ratios obtained by SIMS. αSIMS varies as a function of wt% PbO, requiring two working curves to define the relationship between the $^{206}Pb^+/^{238}U^+$ and $^{207}Pb^+/^{235}U^+$ ratios measured by SIMS vs. the "True" $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$:

$$y_1 = 0.8277 \, x_1^{0.65}$$
$$y_2 = 0.3185 \, x_2^{0.58}$$

where y_1 and y_2 are "True" values and x_1 and x_2 are the ratios $^{207}Pb^+/^{235}U^+$ and $^{206}Pb/^{238}U$, respectively, measured by SIMS.

The application of this technique to unconformity-type uranium deposits in Canada, demonstrates that at the microscale these deposits preserve a temporal record of accretion and break up of supercontinents. Prior to *in situ* analyses, this detailed chronological record was obscured by the wide variability in U-Pb data obtained by micro-drilling and conventional isotopic analyses due to mixing of different generations of minerals. Only in studies that integrated a variety of crystal chemical techniques were these records less obscure. *In situ* U-Pb data demonstrate that uranium deposits can record the timing at which various continent-sized blocks came into existence and their histories of growth.

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