### 4.2.P08

# Impact of organic complexation on Ce(III) oxidation and REE adsorption onto Mn and Fe oxides

#### G. GRUAU, M. DAVRANCHE, O. POURRET, A. DIA

CAREN-CNRS, University of Rennes, France (melanie.davranche@univ-rennes1.fr)

Experiments on the adsorption of rare-earth elements (REE) onto  $MnO_2$  were conducted to evaluate the effects of REE organic complexation on REE(III) adsorption kinetics as well as Ce(III) oxidation rate. Time-series experiments indicate that a stationary exchange equilibrium is reached within less than 10 h when dissolved REE(III) occurs as a free species. By contrast, the steady state is not reached before 20 d when REE are present as humate complexes. Humate complexation also results in a significant decrease of Ce(III) oxidation rates leading to the formation of only very slightly positive Ce anomalies. Adsorption of REE(III)-humate is found to be a complex phenomenon, with an initial stage of fast adsorption (between 0 and 8 d) followed by a desorption episode, the latter occurring in parallel with Ce(III) oxidation.

This complex temporal evolution reflects a modification of the ternary REE(III)-humate- $MnO_2$  surface complex, changing from an initially anionic form, in which the REE(III)-humate complex is bound to the  $MnO_2$  surface through the humate side, towards a cationic form in which this binding occurs through the REE(III) side of the REE(III)-humate complex.

Adsorption experiments of rare-earth elements (REE) onto hydrous ferric oxide (HFO) were also performed. Patterns of partition coefficient obtained from HFO suspensions exhibit a slight positive Ce anomaly and an M-type lanthanide tetrad effect, in contrast with the partitioning between REE(III)humate complexes and HFO, which yields completely flat distribution patterns. The lack of any positive Ce anomaly or M-type lanthanide tetrad effect in the organic experiments seems to reflect an anionic adsorption of the REE-humate complex. Adsorption onto HFO takes place via the humate side of the REE(III)-humate complexes. The oxidation of Ce(III) by Fe(III) and the proportion of surface hydroxyl groups coordinated to REE(III) at the HFO surface are the two most commonly invoked processes for explaining the development of positive Ce anomalies and the M-type tetrad lanthanide effect.

The present results indicate that Ce cannot be used as a reliable proxy of redox conditions, which applies to both organic-rich waters and precipitates formed in equilibrium with humic species-rich waters. Furthermore, despite the development of strongly oxidizing conditions and the presence of Fe and Mn oxides in the aquifer during weathering, these results account for the lack (or insignificant level) of negative Ce anomalies in organic-rich waters.

### 4.2.P09

# Laterization controlled gold occurrence in the Laowanchang gold deposit, Guizhou province, China

YUANGEN YANG, SHIRONG LIU AND ZHISHENG JIN

Institute of Geochemistry, Chinese Academy of Sciences (yangyuangen@hotmail.com)

Mineral composition, chemical components and chemical index of alteration (CIA) of laterites indicated three chemi-cal weathering processes including argillaceous, bauxitic and ferric process can be observed in Laowanchang lateritic profiles; According to the geochemical classification for laterization, the lateritic process in Laowanchang can be attributed to an early stage of laterization.  $K_2O$ ,  $Na_2O$  and CaO components were highly leached during weathering indicating a strong chemical alteration.

Ore forming elements Au, As and Sb varied greatly along the lateritic profiles. Au contents were usually in the range of  $40 \sim 4551 \times 10^{-9}$ . Sb usually was less than 0.1%; while As normally varied in the grade of point numeral percent with a highest value of 1.8%. Au, As, Sb in laterites were obviously higher than those in Dachanceng layer samples. During laterization, enrichment of Au and As were obviously related with the enrichment of Iron, and they usually concentrated in the relatively reductive circumstance, but Sb in the oxidized circumstance.

High REE contents were normally observed in the lateritic profiles, and their LREE to HREE ratios were usually less than 10. REE distribution patterns of lateritic samples were very similar, but significantly different from those of Dachanceng layer samples. Trace element pair diagrams also revealed that great differences existed for large ionic lithophile elements and incompatible elements between lateritic samples and Dachanceng layer samples. Differences for ore-forming elements between laterites and Dachanceng layer samples were also obvious. All these gave supports that material sources for laterites would not directly be from Dachanceng layer rocks but mainly related with Quaternary sediments. Ore forming substances for Laowanchang gold deposit also less directly connected with Dachanceng layer.

TEM-EDX observations testified various gold occurrences in laterites. Gold was observed existing mainly as granular natural gold, but they could be adsorbed by goethite, siliceous or quartz, also by illites and arsenic bearing goethite, which showed the importance of reduction of Iron during laterization.

This study was financially supported by the National Science Foundation Project of China (Grant No: 40073018).