

## Complexation studies of EDTA with $^{99}\text{Tc}$ analogue rhenium

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Technetium-99 ( $^{99}\text{Tc}$ ) is one of the important waste products formed during the nuclear fuel cycle. In oxidising conditions,  $^{99}\text{Tc}$  exists as the highly mobile pertechnetate anion ( $\text{Tc(VII)O}_4^-$ ), which has widespread environmental implications. When present in anoxic environments and in the presence of reducing species, it is expected that an insoluble solid oxide,  $\text{Tc(IV)O}_2$ , will form. Complexation of  $\text{Tc(IV)}$  with man-made and naturally occurring ligands is expected to increase environmental mobility.

The purpose of this investigation was to use a novel technique, Raman spectroscopy, to determine the complexation of rhenium, a non-radioactive analogue for  $^{99}\text{Tc}$ , with ethylenediaminetetraacetic acid (EDTA) under oxic and anoxic conditions. EDTA is a common nuclear waste co-contaminant and has functional groups representative of much larger natural organic molecules.

In oxic and anoxic conditions, perrhenate ( $\text{Re(VII)O}_4^-$ ) and EDTA were combined with HCl to attain pH values of 3.7, 6.5 and 10.3. Raman spectroscopy showed that the EDTA and perrhenate remained unchanged (e.g.  $971\text{cm}^{-1}$  peak characteristic of the Re-O bond in a perrhenate anion was observed) at all pH values, indicating that no complexation had occurred.

Under highly acidic (pH 0.6) and anoxic conditions, *in situ* reduction of  $\text{Re(VII)}$  in the presence of EDTA resulted in an orange-yellow colour solution and a UV-VIS peak at 450nm, indicative of the formation of a  $\text{Re(IV)}$ -complex. Changes in the Raman spectrum of this solution also indicated complexation shifts of a CN stretch (to  $1112\text{cm}^{-1}$ ) and a  $\text{COO}^-$  vibration (to  $1332\text{cm}^{-1}$ ). Other Raman bands of the Re-EDTA complexes were also investigated for complexation shifts and binding mode information.

It has been shown that rhenium complexes to EDTA by *in situ* ligand reduction under very low pH conditions. Binding through the carboxylate and nitrogen groups of a tetradentate EDTA ligand to a mono-oxorhenium core is proposed. It is hypothesised that  $^{99}\text{Tc}$  could complex under less harsh conditions in presence of ligands, which would prevent the formation of the precipitate  $\text{Tc(IV)O}_2$  and hence increase the environmental mobility of  $^{99}\text{Tc}$ .

## $\text{H}_2$ -rich fluids issued from the Kulo Lasi volcano, a new active hydrothermal field recently discovered in the South-West Pacific

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A lot of Back-arc basins (Fidji, Lau, Manus,...) investigated in the last 20 years revealed an intense hydrothermal activity. A new active vent field was recently discovered off-shore the Futuna island in an unexplored area during a French cruise (September 2010) from hydrothermal anomalies detected in the seawater column. High-temperature fluids were collected by the submersible Nautile from active vents located on a volcano (Kulo Lasi caldeira). The fluids exhibit temperatures of  $343^\circ\text{C}$ , pH of 2.36, low  $\text{H}_2\text{S}$  content (1-3 mM), variability in chlorinity (485 to 735 mM) and are enriched in Mg and  $\text{SO}_4$ . Mixing lines of elements vs Mg clearly reveal three types of fluids, all controlled by phase separation. Mg and  $\text{SO}_4$  data in fluids also show a magmatic influence. Silica measurements show that the reaction zone is at a relatively low depth ( $\sim 700$  m). The fluids are poor in  $\text{H}_2\text{S}$  and  $\text{CH}_4$  but enriched in  $\text{CO}_2$  and  $\text{H}_2$  and also contain a lot of organic compounds (see Konn *et al.*, this meeting). The enrichment in  $\text{CO}_2$  is explained by magmatic degassing from arc-magmas very rich in  $\text{CO}_2$  compared to ridge-magmas, as previously shown in many active sites in back-arc basins. The generation of  $\text{H}_2$  is explained by cristallization of the ascending magmatic basalt and by interaction of hot lava with seawater possible during the hydrothermal circulation. The Kulo Lasi fluids are compared to other fluids previously studied in various back-arc basins.