

## Oxidation states change of Ce(III) by microorganism in the presence of Mn(II)

Toshihiko OHNUKI\*<sup>1</sup>, Naofumi Kozai<sup>2</sup>, Yoshinori SUZUKI<sup>1</sup>, Kazuya TANAKA<sup>1</sup>  
<sup>1</sup>JAEA, Tokai, Ibaraki 319-1195, Japan

### Introduction

Ce is one of the trace elements that can be oxidized from III to IV in the environment; and because Ce(IV) is adsorbed more strongly to bacteria and/or soils than other trivalent rare-earth elements (REEs), Ce anomalies in REE patterns often occur in groundwater [1]. Accordingly, bacteria, such as the Mn(II) oxidizing bacteria, may influence the environmental movements of Ce. However, information on such mobilizations of Ce(III) is limited [2]. In this study, we investigated the formation of biogenic Mn oxides by a bacterial strain isolated from the Yunotaki Mn mine, Hokkaido, Japan, and its effect on Ce(III).

### Experimental

#### Biogenic manganese-oxide formation

The BY86 strain of Mn (II) oxidizing bacteria was isolated from surface water at Yunotaki, Hokkaido, Japan, where Mn was mined[3]. This strain oxidizes Mn(II) to Mn(III) and/or Mn(IV). We cultured the bacteria aerobically in Beef-polypeptone (BP) medium containing the following ingredients: beef extract, 3 g L<sup>-1</sup>; polypeptone, 5 g L<sup>-1</sup>; and NaCl, 5 g L<sup>-1</sup>. The bacteria were cultured in 50 ml of the BP medium on a rotary shaker at 30 °C until the optical density (OD) of the medium reached 1 at 600 nm (OD<sub>600</sub>). We termed this medium the precultured medium. We then added stock solutions of 0.1 M Ce(III) and/or 0.1M Mn(II) to it to give solutions of (i) 1 mM Mn(II), (ii) 0.1 mM Ce(III), and (iii) 0.1 mM Ce(III) and 1 mM Mn(II), herein called (i) Mn medium, (ii) Ce medium, and, the (iii) Ce and Mn medium.

We measured the concentrations of Ce and Mn in the solution. For the analyses of oxidation states of Ce and Mn in the solid phases, the solid phases of the Ce medium were separated from the media solutions, and used for XANES analyses.

#### XANES analysis

The oxidation states of Ce and Mn in the medium, in the bacterial cells, and in the Mn-containing precipitates were determined by XANES analysis. XANES spectra of the powder samples of Ce(III)(NO<sub>3</sub>)<sub>3</sub> and Ce(IV)O<sub>2</sub> were used as standards for Ce(III) and Ce(IV), respectively. The Ce L<sub>m</sub>-edge XANES spectra were obtained from the medium, the bacteria, the Mn-containing precipitates, and the standards at beam line 27B in Photon Factory of High Energy Research Organization (Tsukuba, Japan). The energy of XANES spectrum of Ce was calibrated by the energy (≈730 eV) at the first absorption edge in the spectra of Ce in CeO<sub>2</sub>. The Mn K-edge XANES spectra

were measured for Mn-containing precipitates, and for the MnCl<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, and MnO<sub>2</sub> standards. The absorption energy in spectra of Mn was calibrated by the first peak energy of MnCl<sub>2</sub> (≈6552 eV). We collected spectra in the fluorescence mode for all samples using a 7-elements Ge-array detector interfaced to single-channel analyzers. To avoid the oxidation of Ce(III) to Ce(IV), and of Mn(II) to Mn(III) and/or Mn(IV) during transportation of the material and the analyses, the precipitates were sealed in a plastic bag within an outer one containing an oxygen absorbent. We removed the outer bag, made of material that prevents the penetration of gaseous oxygen, just before taking the XANES measurements.

### Results and discussion

In the absence of Mn(II), the concentration of Ce rapidly decreased to 0.03 mM, increased to 0.06 mM, and then remained there. In the presence of Mn(II), the concentration of Ce fell rapidly to approximately 0.015 mM, and then rose to 0.05 mM, and finally declined to 0.005; a black precipitate containing Mn was formed during this last phase. Mn-bearing precipitates also formed in the medium containing only Mn. XANES analysis of the precipitate revealed the presence of Mn(III) and (IV), and Ce (III) and (IV). Ce (III) was detected in solution, and with the bacteria. S-PIXE analyses of the precipitates showed that Ce was associated with Mn, and not with the bacteria. These results suggest that the precipitation of Ce is preceded by its accumulation by the bacterium, followed by its oxidization to Ce(IV) by the Mn(III, IV)-containing precipitates that the bacteria generate.

### References

- [1] Dia, A., et al., *Geochim. Cosmochim. Acta* 64, 4131(2000).
- [2] Moffett, J. W. *Limnol. Oceanogr.*, 39, 1309(1994).

\* ohnuki.toshihiko@jaea.go.jp