

Fungus activity promoted transformation of lanthanides during biooxidation of divalent manganese

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Biogeochemical processes in the subsurface influenced the environmental mobility of actinides [1]. However, the effect of their biological response on lanthanides migration has been unclear. This work compared the transformation of lanthanides during biooxidation of Mn(II) by fungus *Acremonium strictum* KR21-2 under different incubation conditions. A new Ce-binding biomolecule was found to be released from the fungal cell as an adaptive response of *A. strictum* to lanthanides [2]. This biomolecule was not found to associate with any other trivalent lanthanides tested or with Fe. The biomolecule was characterized as c.a. 4700 Dalton (Da) in size, and it contains saccharides.

The Mn(II)-oxidizing fungus *A. strictum* KR21-2 was used. The cultivation medium initially contained 0–1 mmol/L Mn(II), 0–100 µg/L of each lanthanide element, and 0–100 µL spore suspension. In some of the experiments, 0.1–0.3 mmol/L trisodium citrate was added to the medium to increase the solubility of the lanthanides in the medium. During incubation, concentrations of Mn and the 14 lanthanide elements in the supernatant were monitored by inductively coupled plasma mass spectrometry (ICP-MS). After 100 h cultivation, the chemical species of the lanthanides in the liquid phase were analyzed by size exclusion chromatography coupled with UV-Vis spectrophotometric and ICP-MS detection (SEC-UV-ICP-MS), and the oxidation states of Ce in the solid phase were determined by Ce K-edge X-ray absorption near edge structure (XANES) spectroscopy.

In the absence of citrate, more than 99% of the lanthanides were removed from the liquid phase at 24 h. After 32 h, Mn oxide was formed, and the sorbed Ce started to be desorbed into the solution and desorption increased with increasing time (Fig. 1a). From SEC-UV-ICP-MS analysis, a new intense SEC-ICP-MS peak for Ce was observed at a retention time of 15.9 min in citrate-free sample (Fig. 1b). This result suggested that the fungal cell may have released a biomolecule with a retention time of 15.9 min that formed a complex with Ce in solution. The estimated molecular size of this biomolecule was 4700 Da; therefore, we refer to this Ce-binding biomolecule as “CB4700”.

Adding citrate decreased the interaction between lanthanides and fungal cells. As a result, the removed fraction of lanthanides was less than those in the absence of citrate, and increased with the formation of Mn oxide. Neither desorption of Ce nor SEC-UV peak assigned to CB4700 were observed. This result suggests that CB4700 was released from the fungal cell as an adaptive response of *A. strictum* to lanthanides

Fe species were not detected at the retention time where CB4700 appeared (Fig. 2), indicating that the Ce(IV)-binding functional group in CB4700 could be different from siderophores, a well-known iron carrier which could form complex with Ce(IV) [3]; Given that electrostatic interaction between biomolecules and the SEC column affects molecular size estimation, we used an SEC column with a negative surface charge (GL-W540, Hitachi High-Technologies Corporation, Tokyo, Japan) and an SEC column with a positive surface

charge (Superdex 200, GE Healthcare Bio-Sciences AB, Uppsala, Sweden). The molecular size of CB4700 estimated by two columns was similar, suggesting that CB4700 is a neutral molecule; From XANES analysis, a fraction of Ce in solid phase was present in the tetravalent state. Considering other lanthanides (except for Ce) did not bind to CB4700, the XANES results suggest that CB4700 desorbed Ce(IV) from the solid phase.

To our knowledge, this is the first report of the release of a biomolecule with specific affinity for Ce(IV) as an adaptive response of fungi to lanthanides. Considering the geochemical similarity between Ce(IV) and tetravalent actinides. It is reasonable to suggest that metabolically active cells have an important effect on the remobilization of tetravalent actinides, such as Th(IV), U(IV), and Pu(IV), from nuclear waste materials to pore water. The findings of this study will be helpful for understanding lanthanide cycling in the environment, and for long-term management of nuclear waste sites.

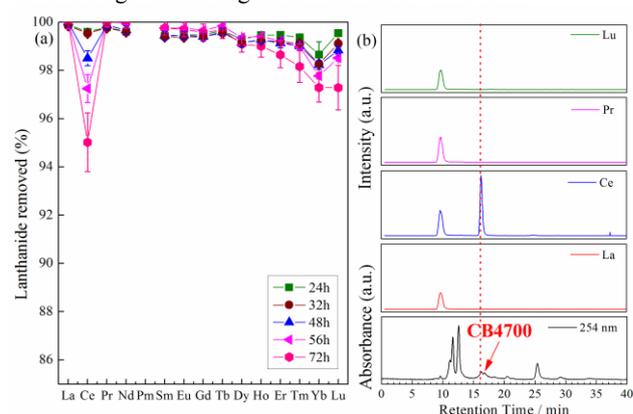


Fig. 1 Changes in (a) lanthanide removal fractions during biooxidation of Mn(II), and (b) SEC-UV-ICP-MS chromatograms of the liquid phase in citrate-free solution after 100 h cultivation.

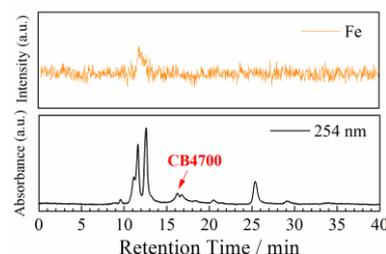


Fig. 2 The relationships between CB4700 and Fe.

References

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