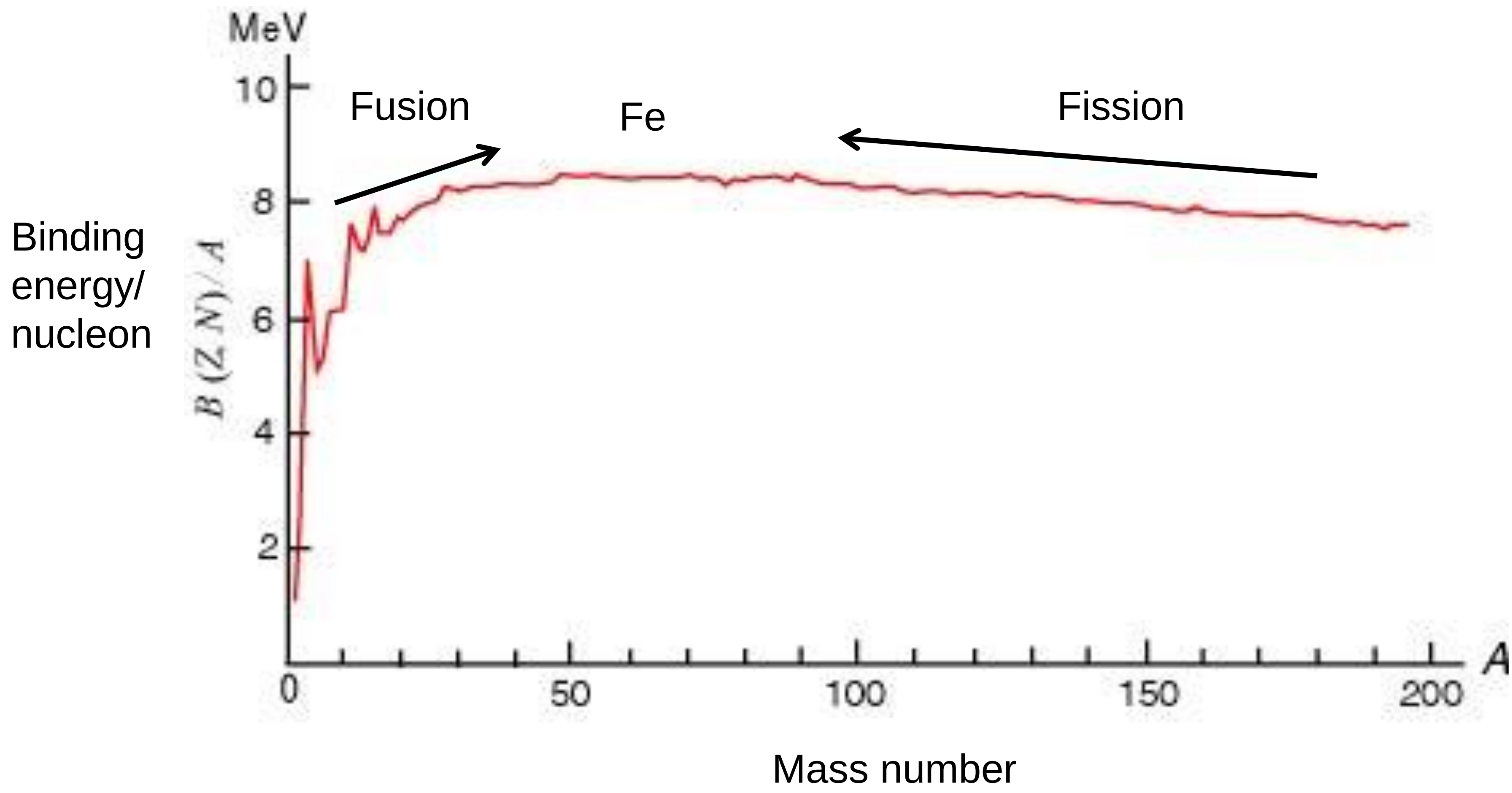
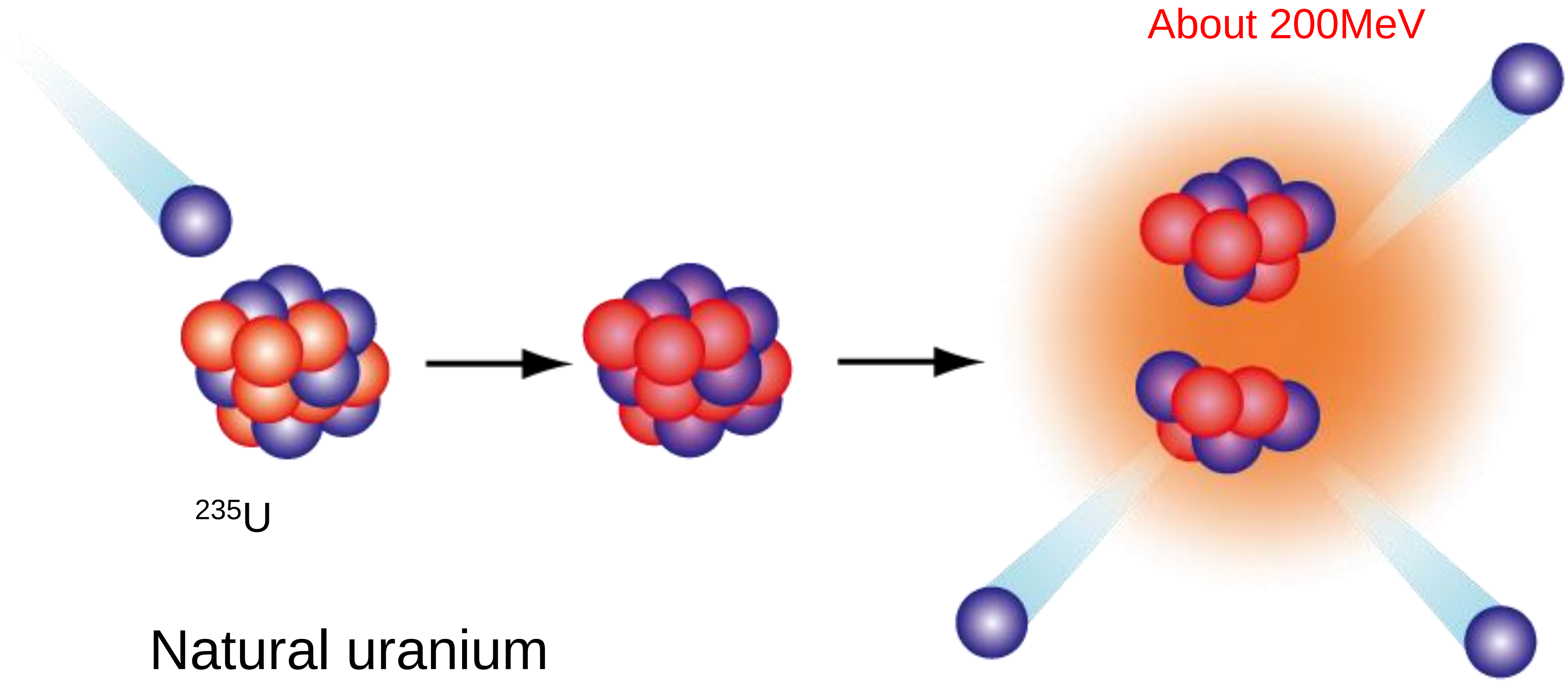
福島第一原子力発電所事故からの復興と高レベル放射性廃液処理に向けた基礎的研究

広島大学
自然科学研究支援開発センター
中島　覚

核子１個あたりの結合エネルギー



誘導核分裂



Natural uranium
^{238}U: 99.275 %
^{235}U: 0.72 %

Enriched ^{235}U is used in nuclear reactor.
^{235}U: 3～5 %

Control material：boron carbide etc.

$${}^{10}_{5}B(n,\alpha)\,{}^{7}_{3}Li$$

福島第一原子力発電所事故の影響

- Influence on environment

  Contaminated→decontamination

  Migration

  Contaminated food→Social influence
- Influence on human body

  Low dose rate exposure
- Social influence

  Social restoration

内容

福島第一原子力発電所事故からの復興

- 移行

  日本海、オホーツク海での移行

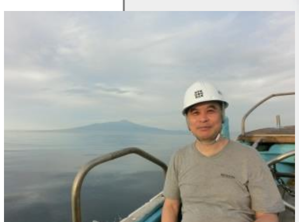
  池周りでの移行

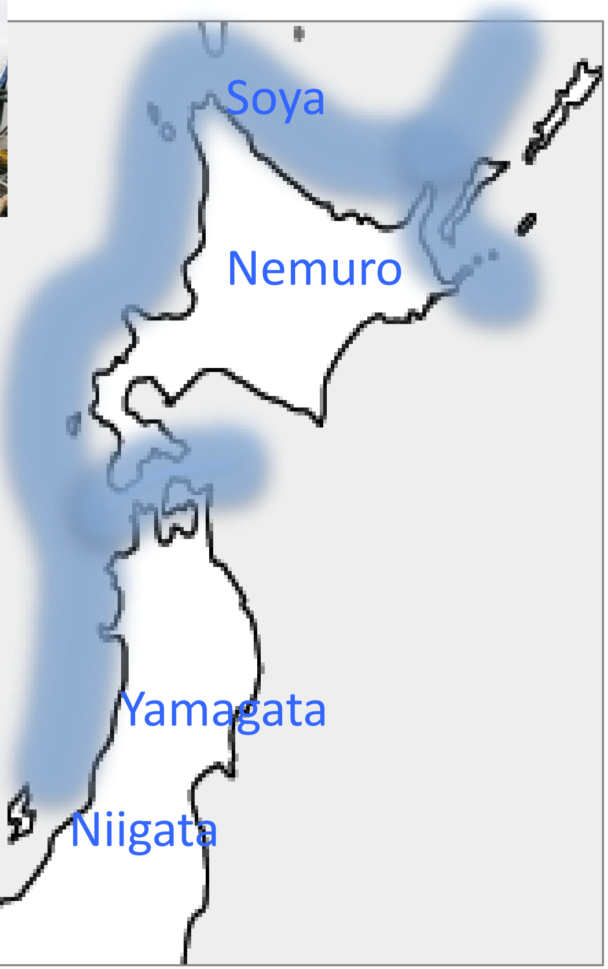
- 米への取り込み

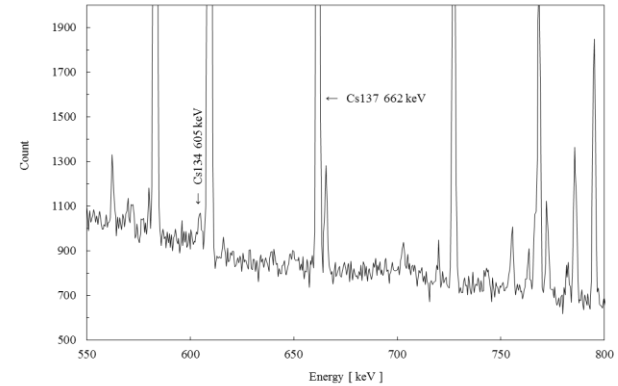
高レベル放射性廃液処理

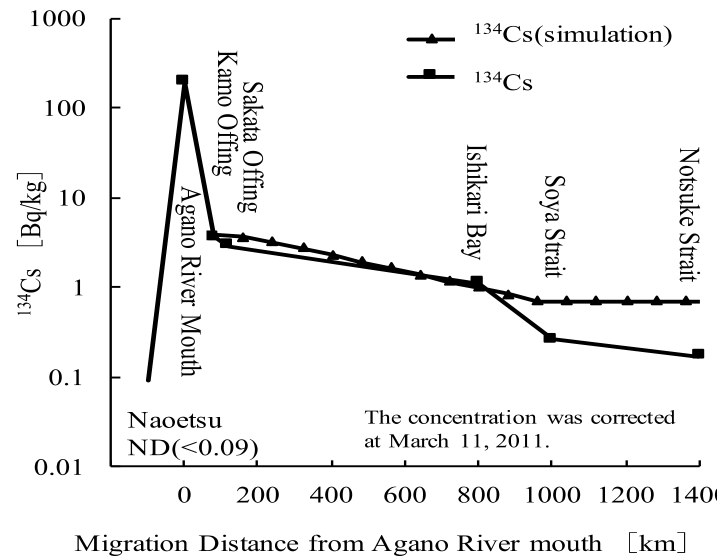
- ランタノイドとマナーアクチノイドの分離

日本海、オホーツク海での^{137}Csの移行









Y. Nabae, S. Miyashita, and S. Nakashima, *Radiation Safety Management*, **15**, 9-14 (2016).
Y. Nabae, S. Miyashita, and S. Nakashima, *Radiation Safety Management*, **16**, 8-12 (2017).
Y. Nabae, M. Tsujimoto, S. Miyashita, and S. Nakashima, *Radioisotopes*, **67**, 573-581 (2018).

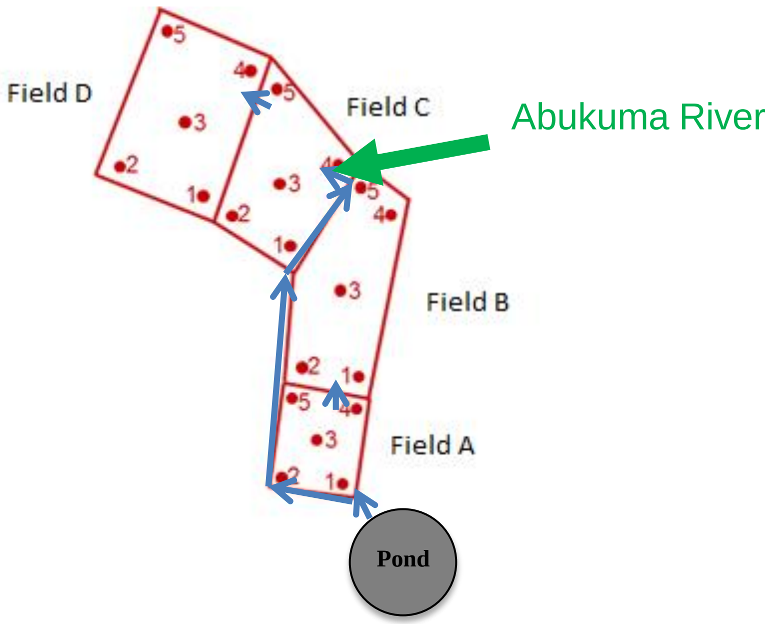
桧原湖での^{137}Csの移行

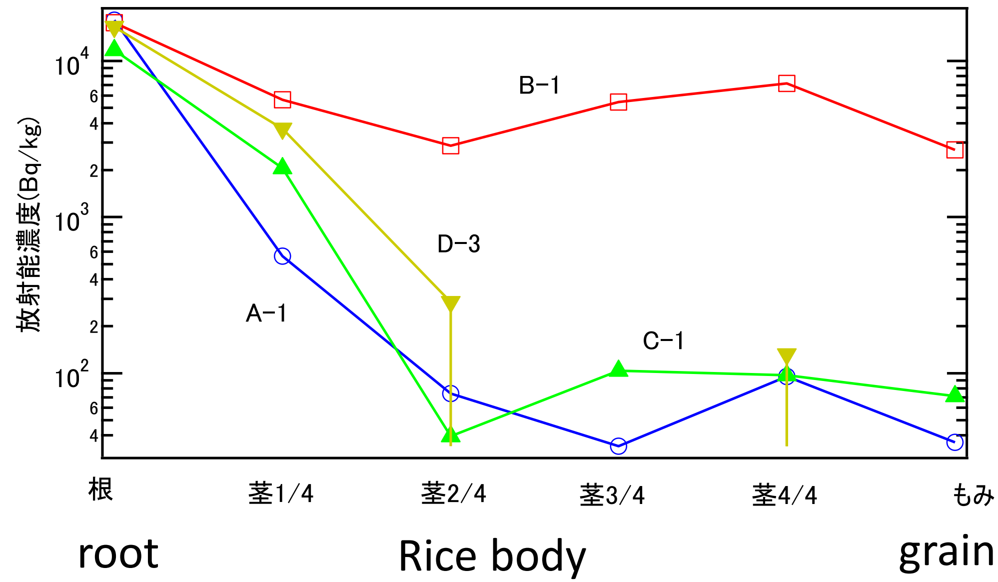
*) Soil concentration data is as of March 11, 2012, Source: http://ramap.jmc.or.jp/map/eng/

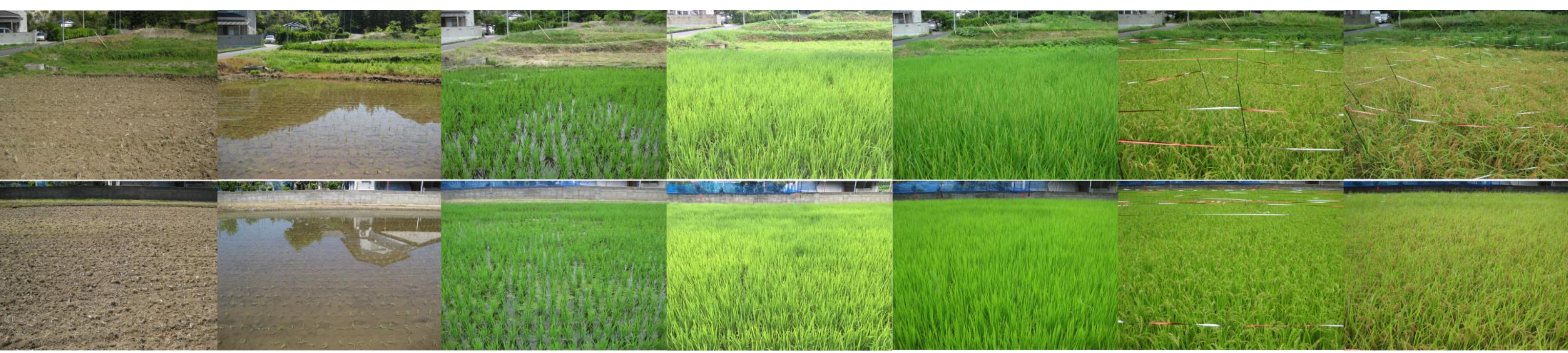
Sampling Area

T. Basuki, S. Miyashita, M. Tsujimoto, S. Nakashima, *J. Radioanal. Nucl. Chem.,* **316**, 1039 (2018).

稲の^{137}Cs吸収



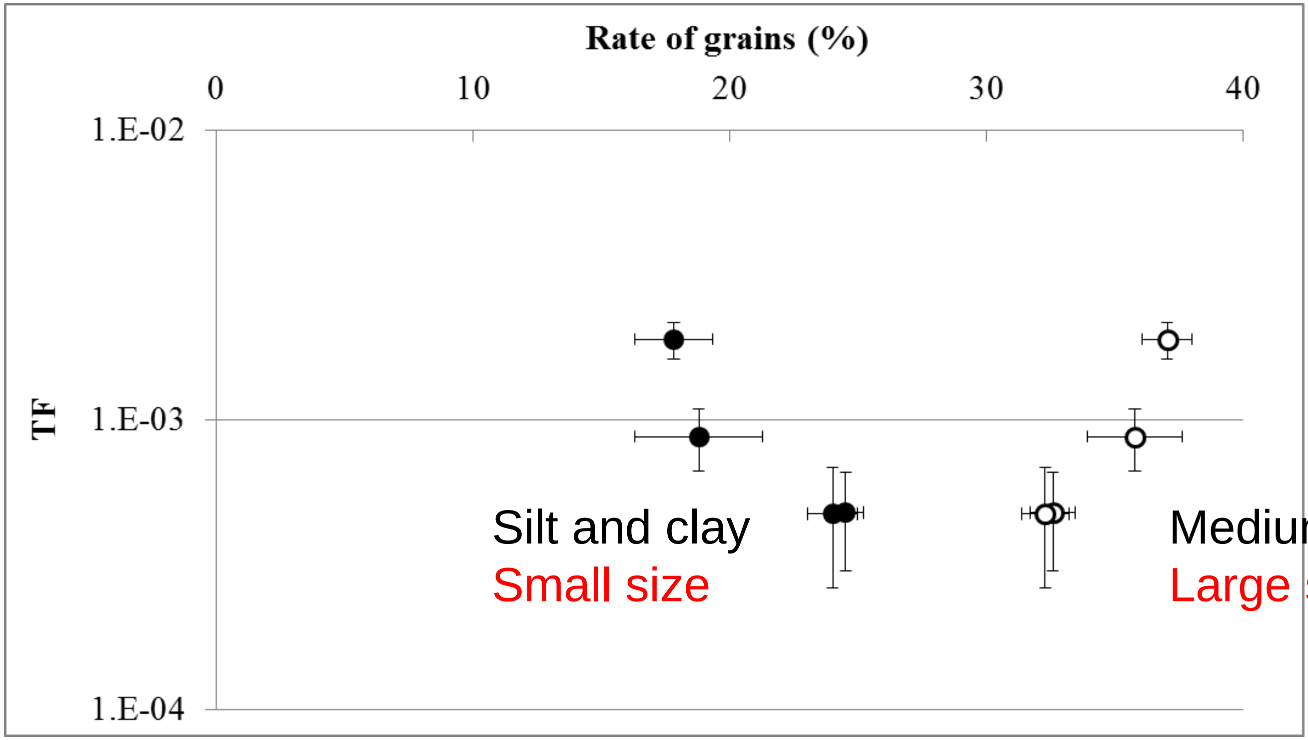




N. Matsuda, S. Nakashima, *Jpn. J. Radiat. Safety Manag.* **13**, 84-91 (2014). (in Japanese).

稲の^{137}Cs吸収

K concentration of Field was low in Field B. Other factors?

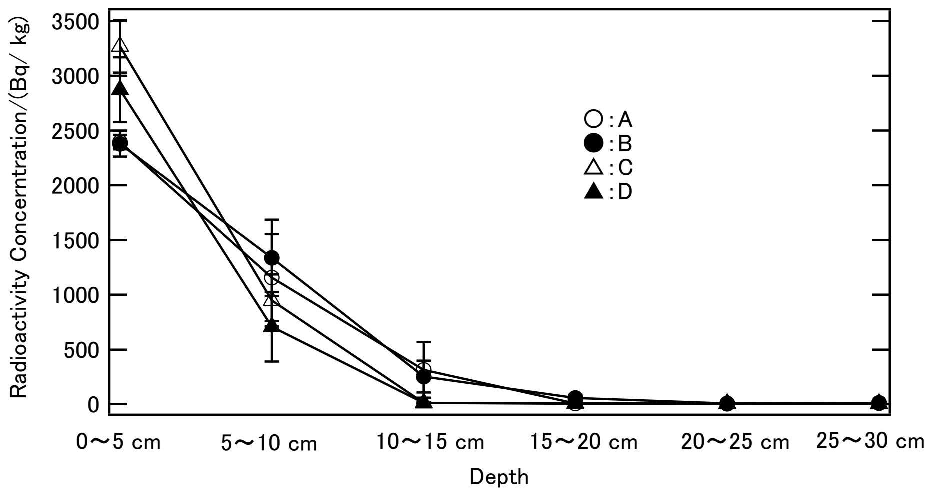


When the ratio of small size soil increases, the transfer factor decreases.

When the ratio of large size soil increases, transfer factor increases.

M. Tsujimoto, S. Miyashita, and S. Nakashima, *Radiation safety Management*, **15**, 1-8 (2016).

稲の^{137}Cs吸収



There is a difference between Fields A, B and Fields C, D.
The radioactivity of ^{137}Cs for 0-5 cm depth is higher in Fields C and D than in Fields A and B, while the radioactivity for 5-10 cm is lower in Fields C and D than in Fields A and B.
^{137}Cs penetrates to more depth in Fields A and B.
⇒Soil situation is different between Fields A, B and Fields C, D.

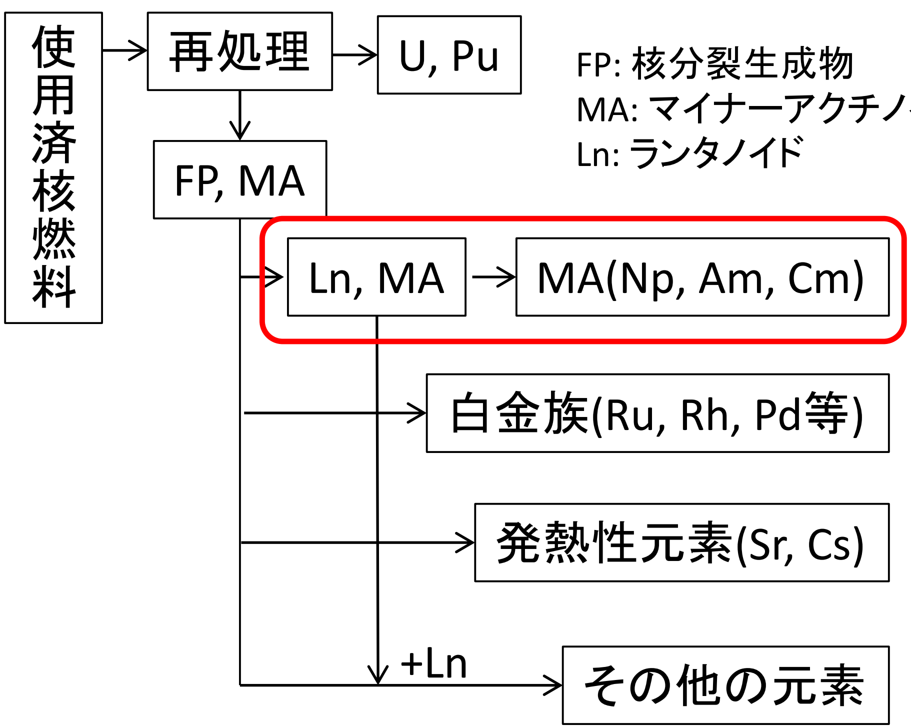
N. T. Hai, M. Tsujimoto, S. Miyashita, and S. Nakashima, *Radioisotopes*, **68**, 13-18 (2019).

Ln/MAの化学分離
Introduction

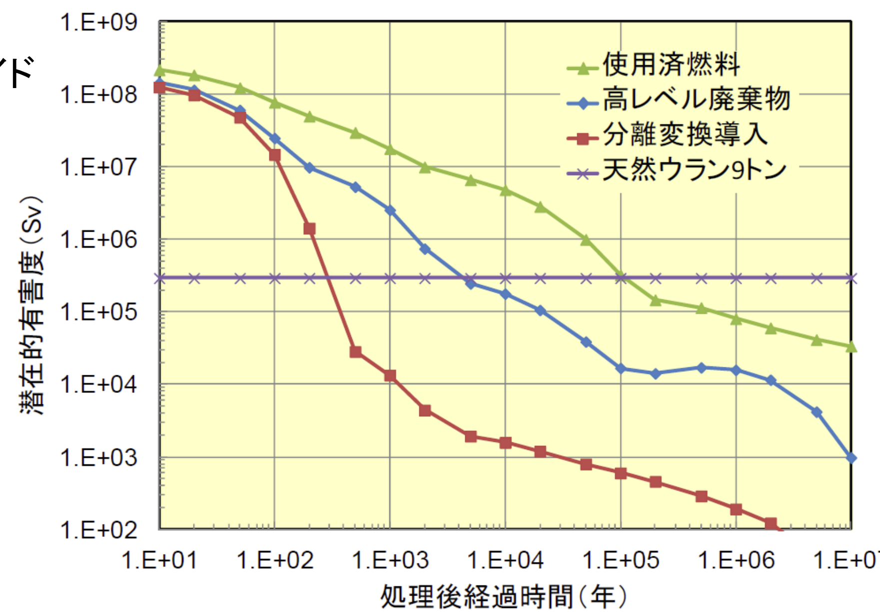
マイナーアクチノイド(MA)の分離・変換処分

分離・変換処分[1]

⇒高レベル放射性廃棄物に含まれる放射性核種をその半減期や利用目的に応じて分離するとともに、長寿命核種を短寿命核種あるいは非放射性核種に変換するための技術

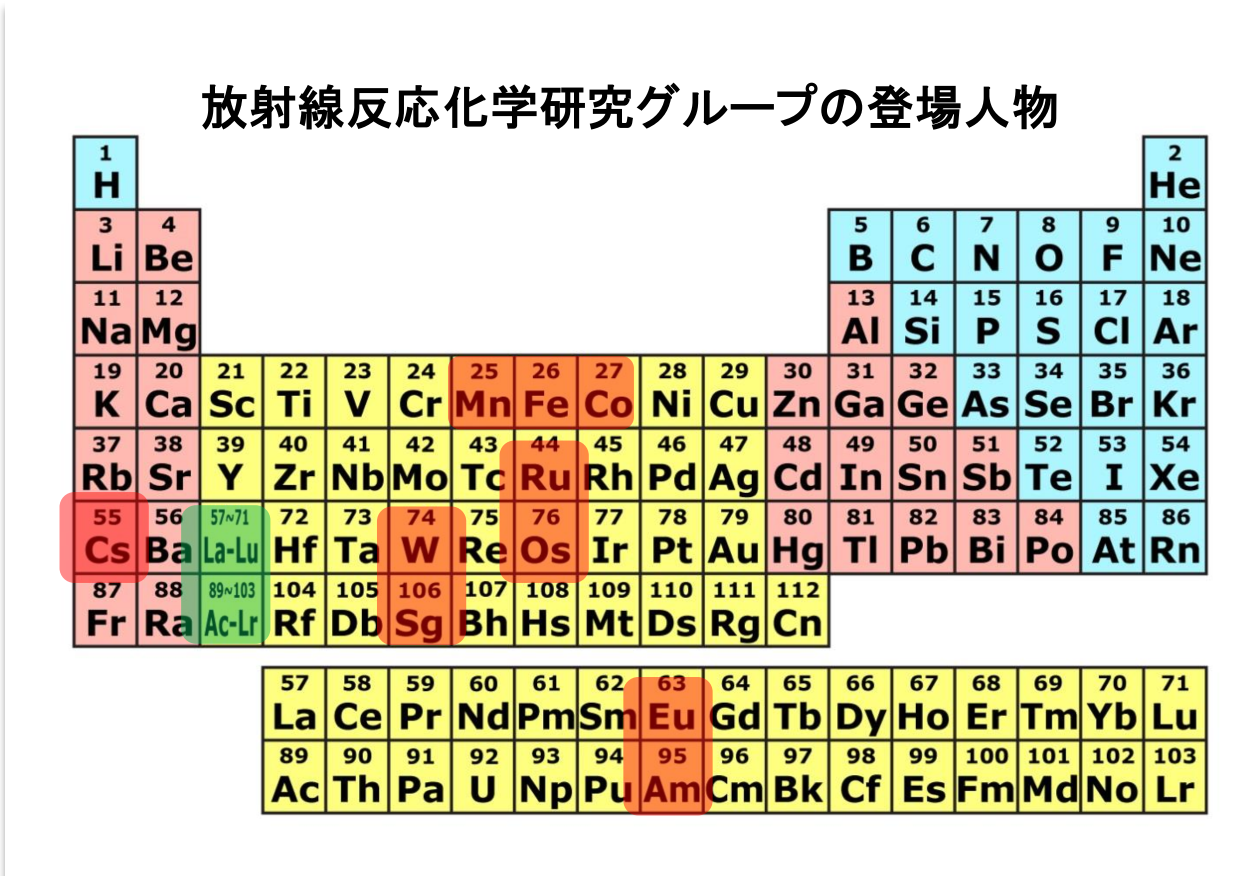


FP: 核分裂生成物
MA: マイナーアクチノイド
Ln: ランタノイド



[1] 大井川 宏之, "エネルギー問題に発言する会", **2012**.

ランタノイドとアクチノイド



ランタノイドの電子配置　[Xe]$4f^n$　$6s^2$

アクチノイドの電子配置　[Rn]$5f^n$　$7s^2$

Ln/MAの化学分離 Introduction

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Ln, MAの類似性
i) 溶液中でIII価が安定
ii) 配位幾何学はほぼ同じ

錯形成によるLnとMAの化学分離

i) 溶媒抽出法

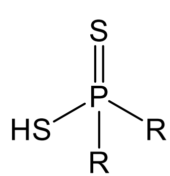
有機相　$n\mathrm{HL}$ ⇅　　$\mathrm{M^{III}L}_n$ ⇅

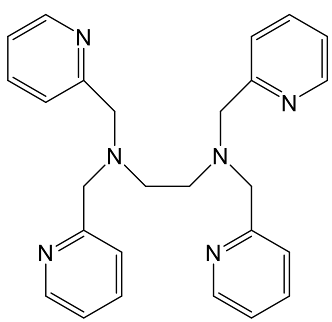
水相　$n\mathrm{HL} + \mathrm{M^{III}aq} \rightleftarrows \mathrm{M^{III}L}_n + n\mathrm{H^+}$

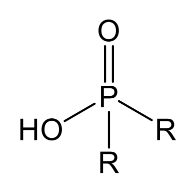
$$D_\mathrm{M} = \frac{[\mathrm{M^{III}L}_n]_\mathrm{o}}{[\mathrm{M^{III}aq}]_\mathrm{w}}$$

$$SF_\mathrm{Am/Eu} = \frac{D_\mathrm{Am}}{D_\mathrm{Eu}} = \frac{[\mathrm{Eu^{III}L}_n]_\mathrm{o}}{[\mathrm{Eu^{III}aq}]_\mathrm{w}}\frac{[\mathrm{Am^{III}L}_n]_\mathrm{o}}{[\mathrm{Am^{III}aq}]_\mathrm{w}}$$

ii) ドナーによるEu/Am選択性の違い







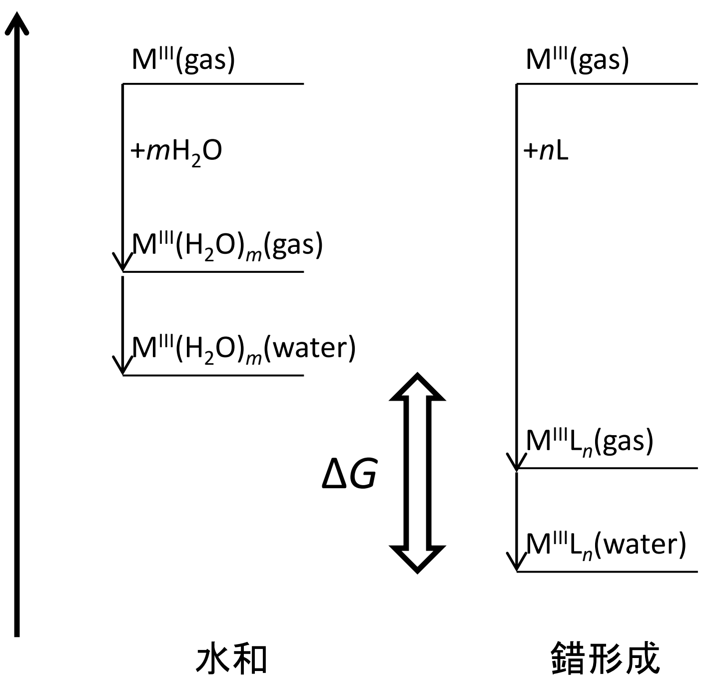
	Sドナー抽出剤 ジチオホスフィン酸	Nドナー抽出剤 TPEN	Oドナー抽出剤 ホスフィン酸
$SF_\mathrm{Am/Eu}$	5.9×10^3	100	5.8×10^{-2}

Ln/MAの化学分離
Introduction

Ln, MAの類似性
i) 溶液中でIII価が安定
ii) 配位幾何学はほぼ同じ

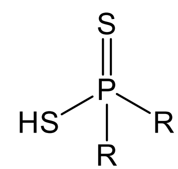
Eu/Am分離に対するDFT研究

i) 熱力学的観点

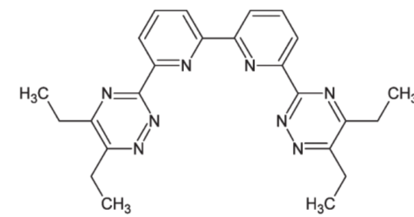


ii) Eu/Am分離挙動

Sドナー抽出剤



Nドナー抽出剤



水溶液中の錯形成エネルギーによって
Ln/MAの安定性を評価

目的①：fブロック錯体の結合状態に対するDFTのベンチマーク研究を行う
目的②：Eu/Amのドナーによる選択性の違いに対する原因を探る

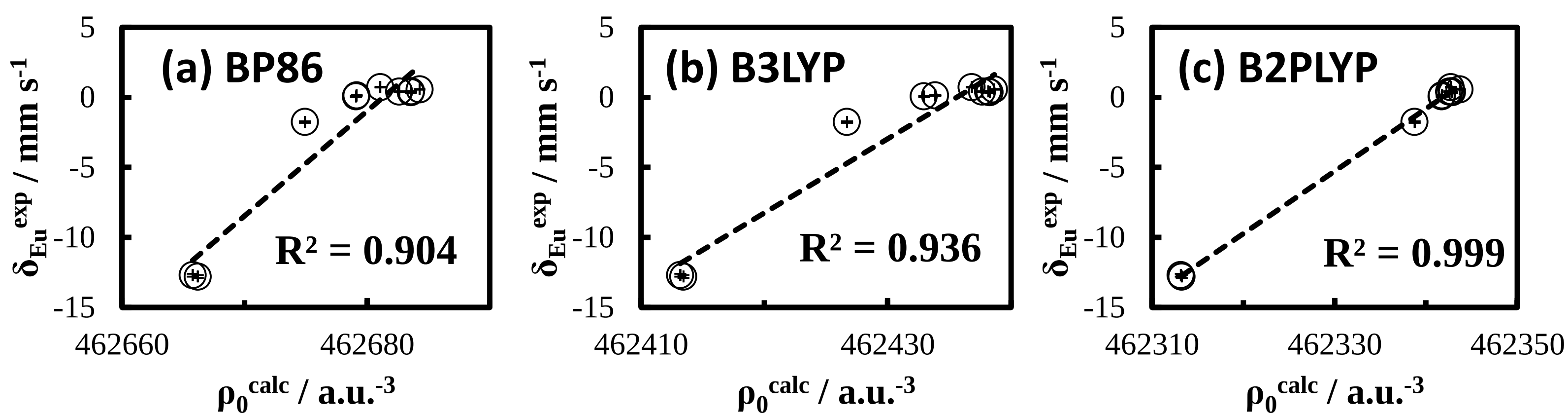
Ln/MAの化学分離　Computational details

^{151}Euベンチマーク研究

$$\delta = \frac{3Ze^2cR^2}{5\varepsilon_0 E_\gamma}\left(\frac{\Delta R}{R}\right)\left(\rho_0^A - \rho_0^S\right)$$

$$\delta^{\mathrm{exp}} = a\left(\rho_0^{\mathrm{calc}} - b\right)$$

Eu complexes	O. S.	$\delta_{\mathrm{Eu}}^{\mathrm{exp}}$ / mm s^{-1}*
[EuCp*$_2$(THF)]	II	-12.8(1) [4.2K]
[EuCp*$_2$]	II	-12.7(1) [4.2K]
[EuCp$_3$(THF)]	III	-1.77(5) [4.2K]
[EuCpCl$_2$(THF)$_3$]	III	0.06(5) [4.2K]
[EuCp(NCS)$_2$(THF)$_3$]	III	0.14(5) [4.2K]
[Eu(acac)$_3$(H$_2$O)$_2$]	III	0.36(4) [4.2K]
[Eu(pta)$_3$(H$_2$O)$_2$]	III	0.42(4) [4.2K]
[Eu(NO$_3$)$_3$(phen)$_2$]	III	0.41(2) [77K]
[EuCl$_3$(phen)$_2$]	III	0.57(2) [77K]
[Eu(NCS)$_3$(bipy)$_3$]	III	0.72(2) [77K]



Std. dev. / mms^{-1}　1.60　1.32　0.20

M. Kaneko, S. Miyashita, and S. Nakashima, *Dalton Trans.*, **44**, 8080-8088 (2015).

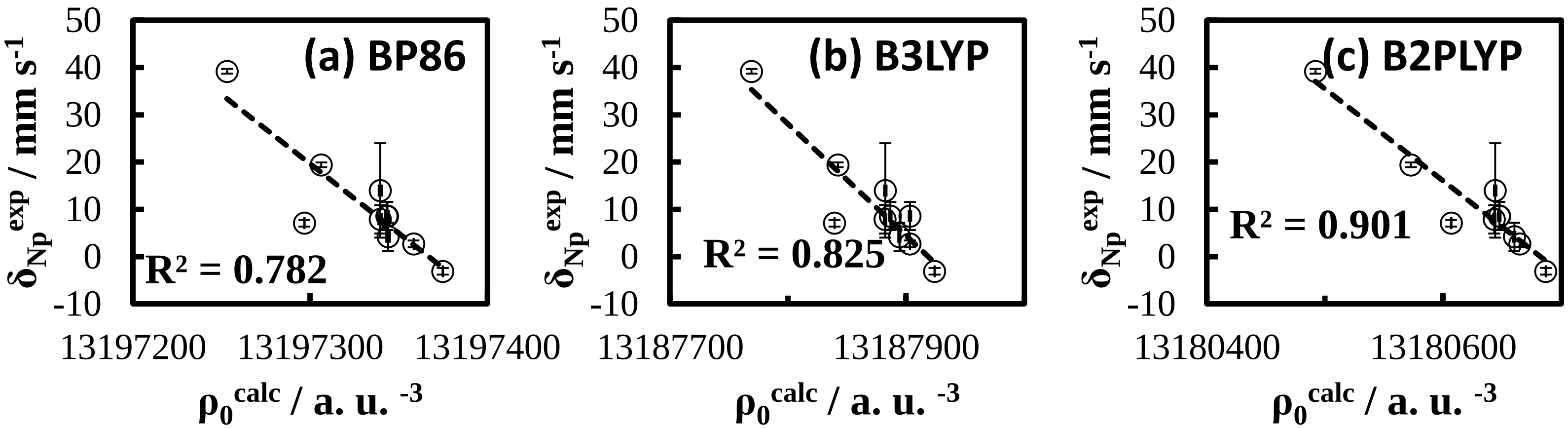
Ln/MAの化学分離　Computational details

^{237}Npベンチマーク研究

$$\delta = \frac{3Ze^2cR^2}{5\varepsilon_0 E_\gamma}\left(\frac{\Delta R}{R}\right)(\rho_0^A - \rho_0^S)$$

$$\delta^{exp} = a\,(\rho_0^{calc} - b)$$

Np complexes	O. S.	δ_{Np}^{exp} / mm s^{-1}*
$[Np^{III}(COT)_2]^-$	III	39.2(5) [4.2K]
$[Np^{IV}(COT)_2]$	IV	19.4(5) [4.2K]
$[Np^{IV}Cp_3Cl]$	IV	14(10) [4.2K]
$[Np^{IV}Cp_3\{OCH(CH_3)_2\}]$	IV	8.6(20) [4.2K]
$[Np^{IV}Cp_3\{OC(CH_3)_3\}]$	IV	8.6(30) [4.2K]
$[Np^{IV}Cp_3\{OCH(CF_3)_2\}]$	IV	7.9(20) [4.2K]
$[Np^{IV}Cp_4]$	IV	7.2(2) [4.2K]
$[Np^{IV}Cp_3(p\text{-}CH_3C_6H_4CH_2)]$	IV	4.2(28) [4.2K]
$[Np^{IV}Cp_3(n\text{-}C_4H_9)]$	IV	2.7(7) [4.2K]
$[Np^{IV}(MeCp)Cl_3(THF)_2]$	IV	-3.1(7) [4.2K]



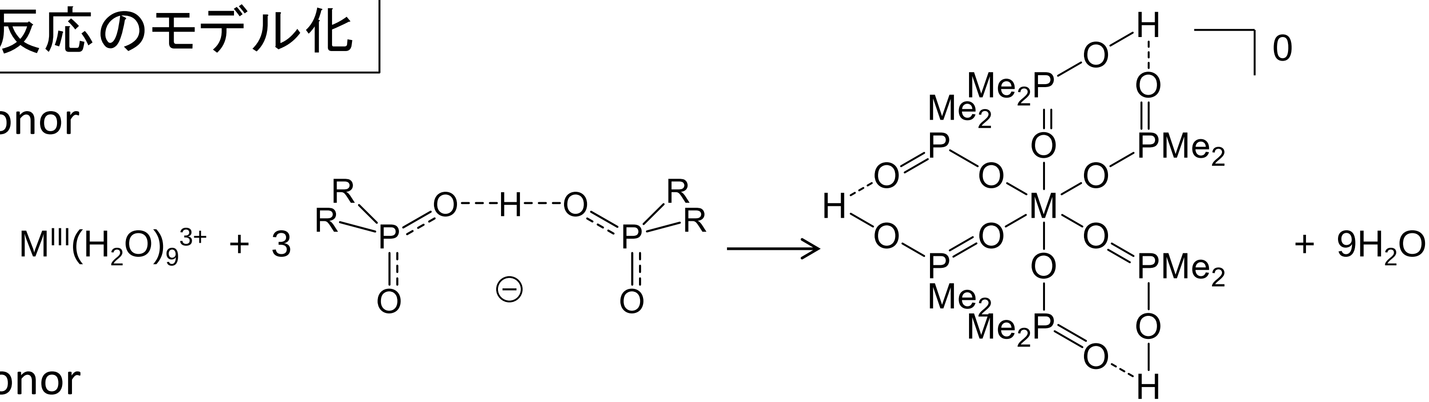
Std. dev. / mms^{-1}	5.17	4.63	3.48

M. Kaneko, S. Miyashita, and S. Nakashima, *Dalton Trans.*, **44**, 8080-8088 (2015).

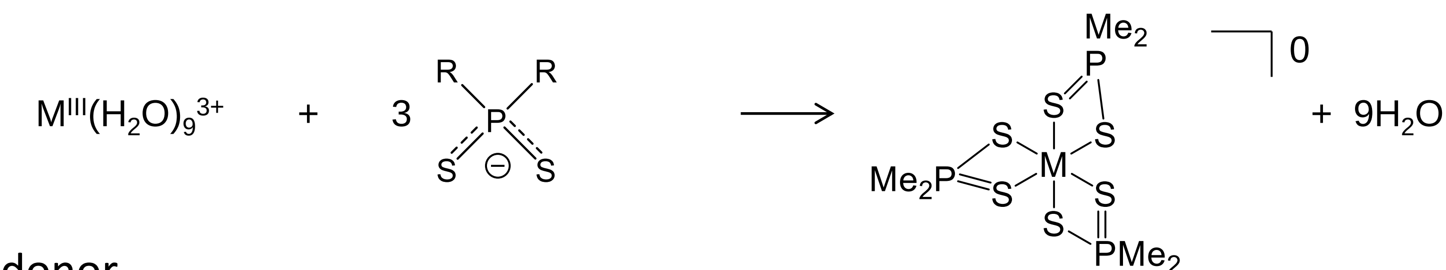
Ln/MAの化学分離
Computational details

錯形成反応のモデル化

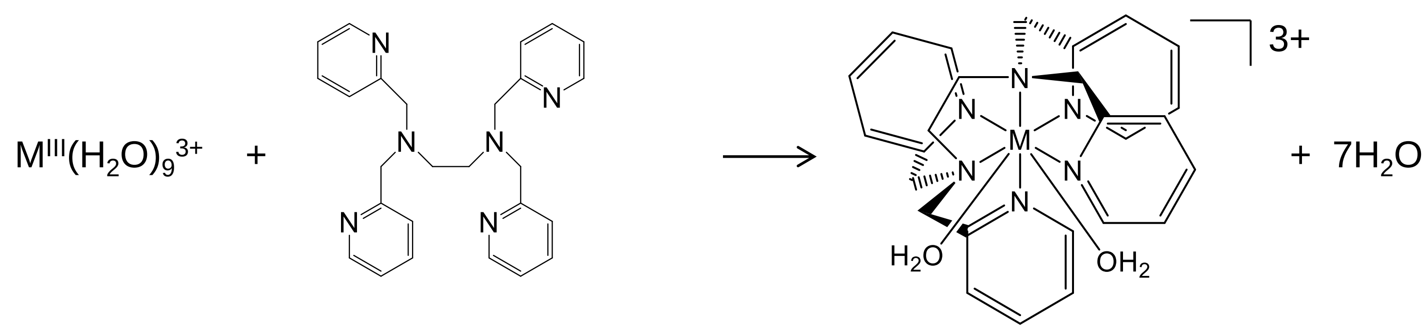
i) O-donor



ii) S-donor



iii) N-donor



Scheme 水溶液中におけるO, S, NドナーによるEu, Am錯体の錯形成反応.

Ln/MAの化学分離
Results

Eu/Am分離挙動の再現

Table 3 Calculated $\Delta\Delta G_{\mathrm{Eu/Am}}$ values obtained by each method

Method	$\Delta\Delta G_{\mathrm{Eu/Am}}$ / kJ mol^{-1}		
	O-donor	S-donor	N-donor
BP86	–20.8	–14.3	–11.8
B3LYP	–22.1	+0.8	–0.1
B2PLYP	–20.9	+23.5	+7.6
Exp.	**–8.1**[3]	**+21.5**[6]	**+11.4**[5]

Exp: $[\mathrm{M}^{3+}]_{\mathrm{aq}} + 3[\mathrm{HL}]_{\mathrm{org}} \rightleftarrows [\mathrm{ML}_3]_{\mathrm{org}} + 3[\mathrm{H}^+]_{\mathrm{aq}}$

Calc : $[\mathrm{M(H_2O)_9}^{3+}]_{\mathrm{gas}} + 3[\mathrm{L}^-]_{\mathrm{gas}} \rightarrow [\mathrm{ML}_3]_{\mathrm{gas}} + 9[\mathrm{H_2O}]_{\mathrm{gas}}$

$$\Delta G_{\mathrm{calc}} = G^{\mathrm{ele}}(\mathrm{product}) - G^{\mathrm{ele}}(\mathrm{reactant})$$
$$\Delta\Delta G_{\mathrm{Eu/Am}} = \Delta G_{\mathrm{calc}}(\mathrm{Eu}) - \Delta G_{\mathrm{calc}}(\mathrm{Am})$$

M. Kaneko, S. Miyashita, and S. Nakashima, *Inorg. Chem.*, **54**, 7103-7109 (2015).

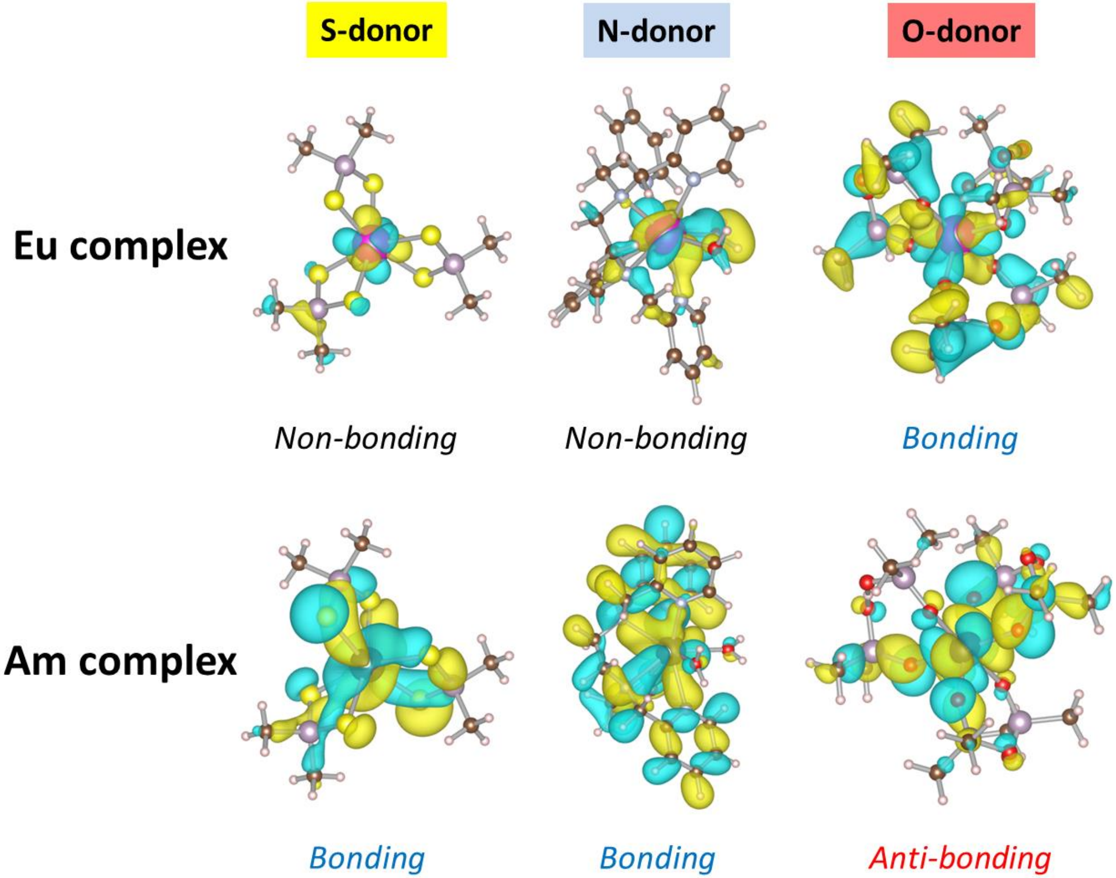
Ln/MAの化学分離

Discussion

Eu/Am分離挙動の再現

ΔG(Eu) – ΔG(Am) (kJ mol^{-1})

	S-donor	N-donor	O-donor
Calc.	**23.5**	**7.6**	**–20.9**
(*Exp.*	*21.5*	*11.4*	*–7.1*)



M. Kaneko, S. Miyashita, and S. Nakashima, *Inorg. Chem.*, **54**, 7103-7109 (2015).

放射線反応化学研究グループ

http://home.hiroshima-u.ac.jp/radichem/