

Annual Report of User's Meeting on
"Condensed-matter Chemistry in Actinides and their
Applications" and
"Production of Medical RIs by Reactor Irradiation"

CCA, KURNS, Kyoto University

Mar. 31, 2023

The originating Section of this publication in the KURNS, Kyoto University was: The CCA
lab. (The laboratory in the field of Condensed-matter Chemistry on Actinides) 2,
Asashiro-Nishi, Kumatori-cho, Sennan-gun, Osaka 590-0494 JAPAN

Annual Report of User's Meeting on
"Condensed-matter Chemistry in Actinides and their Applications" and
"Production of Medical RIs by Reactor Irradiation"
Institute for Integrated Radiation and Nuclear Science (KURNS),
Kyoto University
Published by CCA, KURNS, Kyoto Univ. in Japan
Mar. 31, 2023

Preface

This workshop was co-organized by Prof. H. Yamagami (Kyoto Sangyo Univ.), who is a theoretical researcher of condensed matter physics of actinides, to provide a basis for current and future research activities on actinide science. The actinide science stems from basic research on condensed matter physics and chemistry, to research on nuclear fuel cycle and radioactive waste as its application, and recently to basic research on IF debris and nuclear medicine. The community has held annual workshops at Tohoku University and Kyoto University since 2008. Also, we co-chaired the executive committee of the Actinides International Conference "Actinides2017" which was held in Sendai, Japan, in 2017. This conference was held just prior to the recent "Actinides2023" conference in Denver (June 4-8, 2023), which was originally planned as "Actinides2021" but postponed due to COVID-19.

Our institute (KURNS, Kyoto University) has decided to shut down our KUR reactor in 2026. Based on discussions in Japan, a new research reactor will be built at Fukui, and the institute will participate in its construction and operation of cooperative researches among universities. On the other hand, the future of the Kumatori site, where the institute is currently located, is currently being discussed. Among the discussions, the core of the Kumatori site has gradually been recognized as the hot laboratory, which is expected to play an important role in basic research on actinides, radioactive wastes, and cancer treatments as nuclear research in a broad sense.

Kyoto University and JAEA have been conducting overseas research to contribute to the detailed design of the Fukui Reactor, including visits to the University of Missouri Reactor (MURR) in the United States, the High Flux Isotope Reactor (HFIR) and the Radiochemistry Engineering Development Center (REDC) at Oak Ridge National Laboratory (ORNL), and SHINE Technologies. As the saying goes, a picture is worth a thousand words, it was very meaningful for us to hear in-depth research discussions with many researchers at various sites

during this laboratory visit. When we discussed with them that we would like to share with the Japanese community at the research meeting, all the people we had discussions with agreed to do so, despite the short time between the visit and the lecture. We would like to thank you again for this valuable opportunity.

Since two years before, we have registered the report in the Kyoto University Academic Repository KURENAI to make it available to a wider audience and to preserve it permanently. We hope that the publication of this book in the repository will attract more people, especially young people, to the field of condensed matter chemistry of actinides and its applications.

June, 2023

Tomoo Yamamura

Professor, KURNS, Kyoto Univ.

Preface to the First Publication of the Report of the Topical Meeting on "Topical meeting on Condensed-matter Chemistry on Actinides"

This workshop was organized by Prof. Tomoo Yamamura and his colleagues at the Institute for Integrated Radiation and Nuclear Science, Kyoto University, and the first meeting was held on February 7, 2020. This booklet is a report of the meeting.

Although the new coronavirus infection spread worldwide in these days, it was greatful to hold a meeting with 42 researchers from a wide range of fields in basic research of actinide science, both domestic and overseas.

I would like to express my thoughts on the purpose of establishing this workshop. The main focus of this group is "basic research and its application in actinide science" in a broad perspective, and we will deal with a wide range of research topics with an interest in experiment and theory, basics and applications. It is also a research group where researchers from various research fields such as physics, chemistry, biology, engineering, and medicine come together. The main participants are joint users of the Institute for Integrated Radiation and Nuclear Science, but many other researchers are also attracted by the activities of the group.

I hope that this workshop will provide an opportunity to learn about the latest research results from different fields, to understand each field from a new perspective, and to get feedback for our own research. Furthermore, it would be great if we could create new research themes and collaborations that are cross-cutting and complementary among the fields. In order to achieve the purpose, it is necessary for the meeting to be a place for open academic exchange and discussions, and I hope that you will continue to actively participate. In addition, due to the unique nature of the field of actinide science, there is an urgent need to pass on sustainable technologies and skills and to develop young human resources, and we welcome student-level participation in this workshop.

We look forward to your continued cooperation in making this a successful and open forum for active discussion.

March 23, 2020

Hiroshi Yamagami,

Kyoto Sangyo University

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Chapter 1 Program

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**Agenda of User's meeting on "Condensed-matter Chemistry in Actinides and their Applications" and
"Production of medical RIs by Reactor Irradiation"**

Location: Main Conference Room, Office Building, KURNS, Kyoto University. (Hybrid)

Date	Time (JST)	Chair	Speaker	Affiliation	Title in Japanese (Tentative)	Title in English (Tentative)
Mar. 2	13:00~13:10 (10 min.)		Tomoo Yamamura	Institute for Integrated Radiation and Nuclear Science, Kyoto University	複合研、当該分野の共同利用、施設と将来計画	Combined Research Institute, joint use of the relevant fields, facilities and future plans
	13:10~13:20 (10 min.)		Hiroshi Yamagami	Kyoto Sangyo University	専門研究会の目標	Goals of Specialized Research Groups
	13:25~13:45 (20 min.)	Yamagami	Yoshinori Haga	Advanced Science Research Center, Japan Atomic Energy Agency	ウラン化合物超伝導体UTe2の単結晶育成と電子状態	Single crystal growth and electronic structure of uranium compound superconductor UTe2
	13:45~14:05 (20 min.)		Masahiko Nakase	Tokyo Institute of Technology	次世代再処理に向けたマイナーアクチノイド抽出のための新規溶媒抽出系探索の新しいアプローチについて	On a New Approach to Exploration of Novel Solvent Extraction Systems for Minor Actinide Extraction for Next Generation Reprocessing
	14:10~14:30 (20 min.)	Fukuda	Ayumi Ishii	Teikyo University of Science	希土類ハイブリッド材料が拓く新光機能	New optical functions opened up by rare-earth hybrid materials
	14:30~14:50 (20 min.)		Masanobu Nogami	Kindai University	アクチノイド配位性モノアミド化合物のFPイオンとの錯形成挙動	Complexation behavior of actinyl ion-coordinating monoamide compounds with FP ions
	15:00~15:20 (20 min.)	Kasamatsu	Kenji Shirasaki	IMR, Tohoku University	Ac-228を用いたDGAによる溶媒抽出	Ac-228 solvent extraction by DGA
	15:20~15:40 (20 min.)		Tohru Kobayashi	Actinide chemistry group, Materials Sciences research center, Japan Atomic Energy Agency	複合研の施設供用での成果とSPRING-8 JAEA播磨ラボとの現状について	Achievements in the facility utilization of the Combined Research Laboratory and the current status with the SPRING-8 JAEA Harima Lab.
	15:45~16:05 (20 min.)	Nakase	Yoshitaka Kasamatsu	Graduate School of Science, Osaka University	重アクチノイド、ノーベリウムの化学研究	Recent chemical researches on nobelium
	16:05~16:25 (20 min.)		Takashi Yoshimura	Radioisotope Research Center, Institute for Radiation Sciences, Osaka University	大阪大学放射線科学基盤機構の紹介	Introduction to Institute for Radiation Sciences, Osaka University
	16:30~16:45 (15 min.)	Yamamura	Yoshinori Sakurai	KURNS, Kyoto Univ.	米国ホットラボ視察報告(1)	Report on Survey of Hot Labs and RI Studies in the U.S. (1)
	16:45~17:00 (15 min.)		Hisao Yoshinaga	KURNS, Kyoto Univ.	米国ホットラボ視察報告(2)	Report on Survey of Hot Labs and RI Studies in the U.S. (2)
	17:00~17:10 (10 min.)		Tomoo Yamamura	Institute for Integrated Radiation and Nuclear Science, Kyoto University	施設に関する議論	Discussions on facilities

Mar. 3	8:00~8:05 (5 min.)		Masahiko Nakase	Tokyo Institute of Technology		Opening of 2nd-day Discussions
	8:05~8:30 (25 min.)	Nakase	Greg Piefer	SHINE Technologies, Inc.		Plan and prospect of SHINE Technology
	8:35~8:55 (20 min.)	Shirasaki	Laetitia H. Delmau	Oak Ridge National Laboratory		Overview of the Cf-252 and Pm-147 Production Efforts at ORNL
	9:00~9:20 (20 min.)	Sakurai	Rob Hall	MURR, Missouri University		Recent activities, systems, and facilities of MURR for radiopharmaceutical R&D
	9:25~9:45 (20 min.)	Fukuda	Toro Gonzalez	Oak Ridge National Laboratory		Lanthanide-based and Poly(lactic-co-glycolic acid) Nanoparticles in Targeted Alpha Therapy
	9:50~10:10 (20 min.)	Haga	Julie G. Ezold	Oak Ridge National Laboratory		Radiochemical Processing at Oak Ridge National Laboratory
	10:10~10:30 (20 min.)		Kenji Ishida	Kyoto University	ウラン化合物超伝導体の核磁気共鳴	Nuclear magnetic resonance in uranium compound superconductors
	10:35~10:55 (20 min.)	Yamagami	Hiroki Shishido	Tohoku University	マイナーアクチノイド燃料の CALPHAD 計算に向けた第一原理計算	First-principles calculations for CALPHAD calculations of minor actinide fuels
	10:55~11:15 (20 min.)		Minoru Abe	Hiroshima University	アクチノイド化合物計算に向けた相対論的電子相関プログラム開発	Development of relativistic electron correlation program for calculation of actinide compounds
	11:20~11:40 (20 min.)	Shirasaki	Hiroyuki Kimura	Kyoto Pharmaceutical University	腫瘍を標的としたラジセオラノステイクス創薬と臨床応用	Tumor-targeted radio-ceragnostics drug discovery and clinical application
	11:40~12:00 (20 min.)		Minoru Suzuki	Institute for Integrated Radiation and Nuclear Science, Kyoto University	量子ビーム生体システム解析・応用ユニットの成果	Quantum Beam Bio-Systems Analysis and Application Unit
	12:00~12:20 (20 min.)	Toyama	Tatsuya Suzuki	Nagaoka University of Technology	酸化トリウムの溶解とラジウム分離	Dissolution of Thorium Oxide and Separation of Radium
	12:20~12:30 (10 min.)		Yoshinori Haga	Advanced Science Research Center, Japan Atomic Energy Agency	Concluding Remarks	Concluding Remarks
	14:00~15:00 (60 min.)		Mari Toyama	KURNS, Kyoto Univ.	施設見学 (KUR、HL)	Facility Tour (KUR, HL)

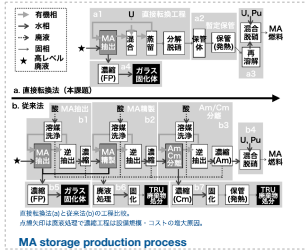
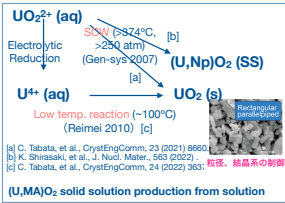
Chapter 2 Presentation Materials

With the permission of the speakers, the materials of their presentations are included here.

I-2. 各分野の状況 f.

Actinide Applications

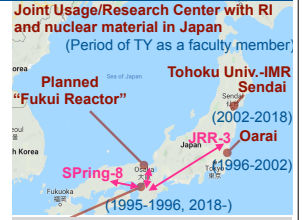
- Reduction of waste volume and potential hazardousness of HLLW
 - The development of MA separation and storage technology
- Mesoscale physical property science research on debris
- Recovery methods for useful elements and nuclides (e.g., $^{228}/^{224}\text{Ra}$ recovery technology from Th)



7

University hot laboratories in Japan

- Five university facilities for RI's and nuclear materials
 - Arising from separate regulation laws in Japan
 - Kyoto Univ.: **KURNS**, Grad. Sch. Eng.
 - Tohoku Univ.: **IMR-Oarai**, **IMR-Sendai**, IMRAM
 - Three **Joint Usage/Research Centers** accept researchers from universities and national institutes
- Active fields in KURNS Hot Laboratory
 - RI utilization
 - Mössbauer spectroscopy
 - Neutron activation analysis (NAA)
- RI supply for medical use *My major fields*
 - Actinide condensed-matter phys./chem.
 - Actinide/MA Applications
- My activities:
 - Annual meeting on Actinides/RIs (2006-, available for download, For FY2023: Mar 2-3)
 - Actinides 2017@Sendai (Co-Executive Committee Chair)



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Discussion of operational management (image)

- Safety Management and Open Lab
- Temporarily controlled area: Highly sensitive equipment for frontier research
- Enhancement of hot biological research capabilities



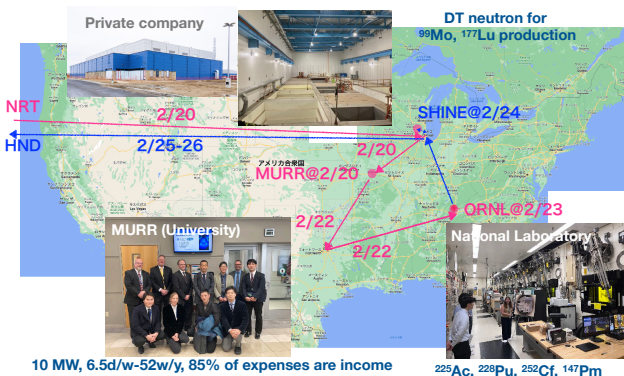
Co-Creation Center (proposed) "Frontier Analysis Center"

- Characteristic measurement equipments: very useful for users in Japan
- Operation with the Fukui Reactor as a complementary facility

「高感度装置」の例

分析内容	核種の同定、定量	配位子構造、ラベリング	表面・元素	低温構造	表面の原子付着・配列状況	化合物構造
装置	ICP-MS/MS	NMR	SEM-EDX	(Cryo-)TEM	STM/AFM	単結晶構造解析
装置イメージ						
用途	核医薬、デブリ、MA	核医薬、デブリ	物質	物質、生命	廃炉、物質	核医薬、デブリ、アクチノイド
研究例	Lu-177の比較射能	Np, Pu, Ac, Am	廃炉、デブリ、化合物の形状、元素分析	U60, U24		

U.S. Research Reactor and Hot Laboratory Survey for Detailed Design of a New Research Reactor (2023/2/20-26)



2.2 H. Yamagami (Kyoto Sangyo Univ.)

Goals of Specialized Research Groups

Users meeting on Condensed-matter Chemistry in Actinides and their Applications

First Meeting : 2020年2月7日 京大複合研 事務棟大会議室 9:35-9:50
 Second Meeting: 2021年2月10日 zoom会議 9:35-9:50
 Third Meeting : 2022年3月3日4日 zoom会議 10:00-15:00
 Fourth Meeting : 2023年3月3日2日 hybrid会議 10:00-15:00

専門研究会の目標 (Goals of Specialized Research Groups)

「アクチノイドの物性化学とその応用」の開催趣旨

京都産業大学 理学部 物理科学科 山上 浩志
 (Kyoto Sangyo University, Hiroshi Yamagami)

本研究会の趣旨 (Perspectives of this meeting)

平成31年度 京都大学複合原子力科学研究所研究会の公募に採択
 趣旨：本研究会は、**複合原子力科学研究所の共同利用の一環として行うもので、複合原子力科学研究所における研究及び原子炉に関するテーマについて開催**

「専門研究会」= テーマにこだわらない一般の研究会で、**プロジェクト研究に向けた研究課題を提案する研究会も含む。**



- (提案)：(1) 研究テーマとして、**広い意味でのアクチノイドの物性化学 (科学) の基礎研究とその応用**
 (2) 実験と理論、および基礎と応用を意識した研究
 (3) 物理、化学、生物、工学、医学などの様々な**異分野の横断的および相補的研究**および**創出**
 (4) **人材育成、および技術技能の継承**に向けた**施策や枠組み**
 (5) オープンな交流の場を提供し、**情報交換と学術的議論**

- 注意事項：
 1. 講演には共同利用研究者 (所属・学生を含む) の発表が半数程度含まれること。
 2. 講演において共同利用研究成果または今後の研究計画等について報告
 3. 共同利用研究活性化のための意見・要望等をまとめる総合討論時間を設ける。

会議のスケジュール (Meeting Schedule)

Date	Time (JST)	Chair	Speaker	Affiliation	Title in Japanese (Thematic)	Title in English (Thematic)
Mar 2	13:00-13:15 (15 min)		Tomoji Yamamura	Institute for Integrated Radiation and Nuclear Science, Kyoto University	報告書、施設概要の紹介、出席者名簿	Combined Research Institute, joint use of the relevant facilities, facilities and future plans
	13:15-13:30 (15 min)		Hiroaki Yamagami	Kyoto Sangyo University	報告書の紹介	Goals of Specialized Research Groups
	13:30-13:45 (15 min)	Yamagami	Yoshinori Hagi	Advanced Science Research Center, Japan Atomic Energy Agency	アクチノイドの物性化学とその応用	Single crystal growth and electronic structure of actinide compound
	13:45-14:05 (20 min)		Masahito Nakase	Sajyo Institute of Technology	アクチノイドの物性化学とその応用	On a New Approach to Exploration of Novel Actinide Oxidation States for Heavy Actinide Extraction for Next Generation Reprocessing
	14:10-14:30 (20 min)		Fukuda	Ajuntai Ltd.	アクチノイドの物性化学とその応用	New optical functions opened up by research on actinide
	14:30-14:50 (20 min)		Masaru Kobayashi	Kinki University	アクチノイドの物性化学とその応用	Competition behavior of actinide ion complexation with humic substances
	15:00-15:30 (30 min)		Kaemitsu	Kyushu University	アクチノイドの物性化学とその応用	Act-238 actinide extraction by DGA
	15:30-15:45 (15 min)		Takuro Kobayashi	Actinide Chemistry Group, National Institute of Advanced Industrial Science and Technology	アクチノイドの物性化学とその応用	Achievements in the facility utilization of the Combined Research Laboratory and the current status with the SPTR@JAEA, HANARO Lab.
	15:45-16:05 (20 min)		Nakase	Yamaguchi University	アクチノイドの物性化学とその応用	Recent chemical researches on neptunium
	16:05-16:25 (20 min)		Takemi Yashima	Radiation Research Center, Institute for Radiation Sciences, Osaka University	アクチノイドの物性化学とその応用	Introduction to Institute for Radiation Sciences, Osaka University
	16:30-16:45 (15 min)		Yamamura	KURNS, Kyoto Univ.	アクチノイドの物性化学とその応用	Report on Survey of HPL Lab and RI Facility in HANARO
	16:45-17:00 (15 min)		Hideo Yoshizawa	KURNS, Kyoto Univ.	アクチノイドの物性化学とその応用	Report on Survey of HPL Lab and RI Facility in HANARO
	17:00-17:15 (15 min)		Tomoji Yamamura	Institute for Integrated Radiation and Nuclear Science, Kyoto University	施設に関する議論	Discussions on facilities

2 opening remarks + 11 talks

March 3

Mar 3	Time (JST)	Chair	Speaker	Affiliation	Title in Japanese (Thematic)	Title in English (Thematic)
	8:00-8:05 (5 min)		Masahito Nakase	Sajyo Institute of Technology		Opening of 2nd-day Discussions
	8:05-8:30 (25 min)		Nakase	Org. Packer	SHINE Technologies, Inc.	Plan and prospect of SHINE Technology
	8:30-8:55 (25 min)		Shimizu	Lawless W. Dennis	Oak Ridge National Laboratory	Production of Pu-241 and Cf-252
	9:00-9:20 (20 min)		Sakurai	Robi Hall	MURR, Missouri University	Recent activities, systems, and facilities of MURR for radiopharmaceutical (RAD)
	9:20-9:45 (25 min)		Fukuda	Toru Gonozaki	Oak Ridge National Laboratory	Lanthanide based and Polyactinide-co-oligoacetic acid Neptunium in Targeted Alpha Therapy
	9:50-10:10 (20 min)		Hagi	John S. Ezzold	Oak Ridge National Laboratory	Radiochemical Processing at Oak Ridge National Laboratory
	10:10-10:30 (20 min)		Kariji Ichikawa	Kyoto University	ウラン化合物の放射線効果の調査	Nuclear magnetic resonance in uranium compound superconductors
	10:35-10:55 (20 min)		Yamagami	Hokkaido University	アクチノイドの物性化学とその応用	First-principles calculations for CALPHAD calculation of minor actinide fate
	10:55-11:15 (20 min)		Miyataki	Hiroshima University	アクチノイドの物性化学とその応用	Development of materials, electron-competition program for separation of actinide compounds
	11:20-11:40 (20 min)		Shimizu	Hiroaki Kimura	Kyoto Pharmaceutical University	Tumor-targeted radio-conducting drug discovery and clinical application
	11:40-12:00 (20 min)		Miyataki	Suzuki	Institute for Integrated Radiation and Nuclear Science, Kyoto University	アクチノイドの物性化学とその応用
	12:00-12:20 (20 min)		Byama	Takayuki Suzuki	Nagasaki University of Technology	アクチノイドの物性化学とその応用
	12:20-12:30 (10 min)		Yashima	Hagi	Advanced Science Research Center, Japan Atomic Energy Agency	Concluding Remarks
	14:00-15:00 (60 min)		Mori Syoma	KURNS, Kyoto Univ.	施設見学 (KURNS, H4)	Facility Tour (KURNS, H4)

12 talks + 1 concluding remarks

First Meeting : 2020年2月7日 京大複合研 事務棟大会議室 9:35-9:50

共同利用研究活性化のための意見・要望等の総合討論

物理、化学、生物、工学、医学などの様々な異分野の横断的および相補的研究および創出 (例えば、実験と理論、基礎と応用、物理と化学、医学と工学など)

人材育成、および技術技能の継承に向けた施策や枠組み (原子力をキーワードにした場合)

オープンな交流の場を提供し、情報交換と学術的議論 (原子力関連研究に関して、研究者は分散しているので、共同研究体制が必要)

アフターコロナ： エネルギー問題、医薬関連、アクチノイド科学

ご静聴ありがとうございます！

オープンで活発な議論をお願いします。

Thank you for your attention!
 We would appreciate an open and active discussion.

2.3 Y. Haga (ASRC, JAEA)

Single crystal growth and electronic structure of uranium compound superconductor UTe_2

Single crystal growth and electronic structure of uranium compound superconductor UTe_2

Y. Haga (JAEA)

ウラン化合物超伝導体 UTe_2 の単結晶育成と電子状態

日本原子力研究開発機構 (東海)
先端基礎研究センター
芳賀芳範

keywords: Heavy Fermion (重い伝導電子)
Electronic specific heat 伝導電子の比熱: 有効質量 (通常 1 mJ/Kmol at 1K)

f-electron Heavy Fermion superconductors			
compound	T_c (K)	C_v / T (mJ/K ² mol)	T_m (K)
1979 CeCu ₂ Si ₂	0.5	~ 1000	complex
UPt ₃	0.45, 0.55	500	5 (fluctuating)
UBe ₁₃	0.9	1000	< 0.01
URu ₂ Si ₂	1.4	80	17.5
UPd ₂ Al ₃	2	145	14.3
UNi ₂ Al ₃	1	300	4
CeIn ₃ (p), CePd ₂ Si ₂ (p), CeRh ₂ Si ₂ (p)			
2001 CeCoIn ₅	2.3	500	< 0.01
CeRhIn ₅ (p)			
CeIrIn ₅	0.4	500	< 0.01
2002 PuCoGa ₅	18.5	70	< 5
PuRhGa ₅	8.5	70	< 0.1
URhGe	0.15	150	10 (ferro)
CePt ₃ Si	0.5	300	2.3
PrOs ₄ Sb ₁₂	1.5	~ 500	< 0.1
CeRhSi ₃ (p), CeIrSi ₃ (p), CeCoGe ₃ (p), UIr (p)			
2006 NpPd ₅ Al ₂	4.9	200	< 0.1
2007 UCoGe	0.8	150	3 (ferro)
2019 UTe_2	1.6 - 2.1	120	high field phase

Unusual SC phase diagram

Ran et al., Science **365**, 685 (2019)

(d) UTe_2 H || b Rosuel et al., arXiv:2205.04524v3

Ran et al., Nature Phys. **15**, 1250 (2019)

Kinjo et al., Phys. Rev. B **2023**

Introduction: Sample dependence of UTe_2

Rosa et al., Commun. Mater. (2022) 3:33.

D. Aoki, ..., YH arXiv:2206.01363

Cairns et al., J. Phys. Condens. Matter **32** (2020) 415602.

U-Te binary phase

Okamoto, H. Te-U (tellurium-uranium). J. Phase Equilibria **14**, 129-130 (1993).

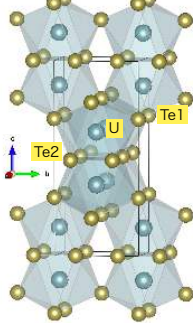
U-Te binary phase

Okamoto, H. Te-U (tellurium-uranium). J. Phase Equilibria **14**, 129-130 (1993).

Single-crystal XRD

Crystal structure (UTe₂-type, Immm) confirmed for both NS and SC samples.

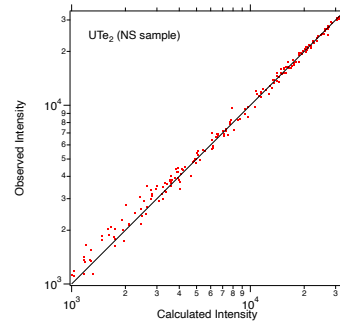
	NS sample	SC sample
Lattice parameters		
<i>a</i>	4.1600(2)	4.1618(5)
<i>b</i>	6.1219(4)	6.1355(7)
<i>c</i>	13.9476(9)	13.9698(13)
Fractional coordinates		
U <i>z</i>	0.13545(5)	0.13520(4)
Te1 <i>z</i>	0.29755(5)	0.29780(10)
Te2 <i>z</i>	0.24895(5)	0.24910(3)
Eq. iso. atomic disp. <i>B</i> _{eq}		
U	0.687	0.513
Te1	0.562	0.576
Te2	0.515	0.529
Residuals (all data)		
<i>R</i> ₁	0.0222	0.0309
<i>wR</i> ₂	0.0564	0.0586



Y. Haga et al., J. Phys.: Condens. Matter 34 (2022) 175601.

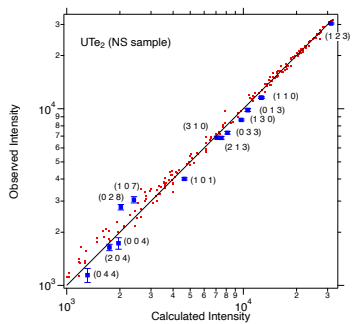
Single-crystal XRD

Showing $I/I_{max} < 0.1$



Single-crystal XRD

Showing $I/I_{max} < 0.1$

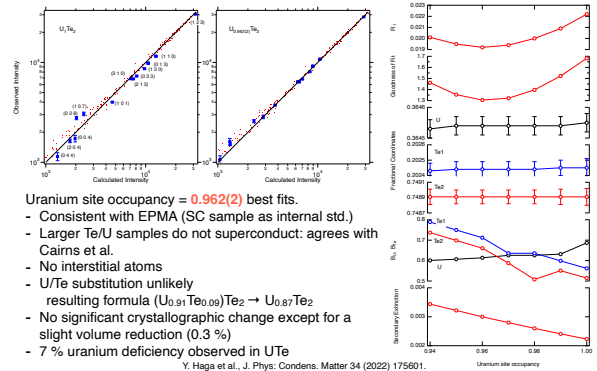


Strongly deviating reflections consist from strong F_U and F_{Te} but cancel each other.

Resulting (weak) intensity is sensitive to

- B_{eq} difference (corrected)
- site occupancy

NS sample is strongly U deficient

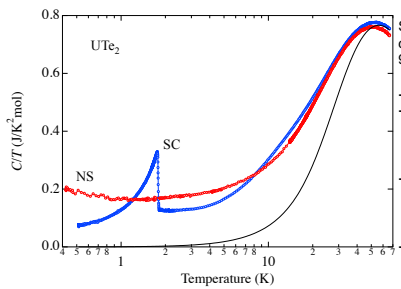


Uranium site occupancy = 0.962(2) best fits.

- Consistent with EPMA (SC sample as internal std.)
- Larger Te/U samples do not superconduct: agrees with Cairns et al.
- No interstitial atoms
- U/Te substitution unlikely resulting formula $(U_{0.91}Te_{0.09})Te_2 \rightarrow U_{0.87}Te_2$
- No significant crystallographic change except for a slight volume reduction (0.3%)
- 7% uranium deficiency observed in UTe

Y. Haga et al., J. Phys.: Condens. Matter 34 (2022) 175601.

Specific heat



SC sample prepared with composition 1.11:2
950/850 temperature gradient

- Sharp single SC transition
- Relatively high $T_c = 1.8$ K
- Highest $T_c = 2.1$ K from recent crystal

- NS sample shows quite different behavior up to high temperature.

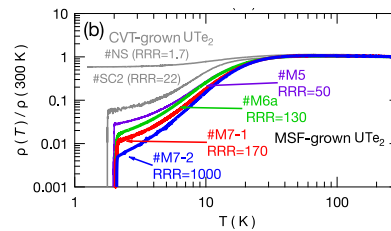
Both SC and NS samples have extra electronic/magnetic contributions (Debye model: black line)

Molten salt flux growth

PHYSICAL REVIEW MATERIALS 6, 073401 (2022)

Single crystal growth of superconducting UTe₂ by molten salt flux method

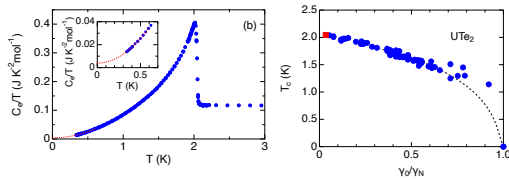
H. Sakai¹, P. Opletal¹, Y. Tokiwa¹, E. Yamamoto, Y. Tokunaga¹, S. Kambe, and Y. Haga¹
¹Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan



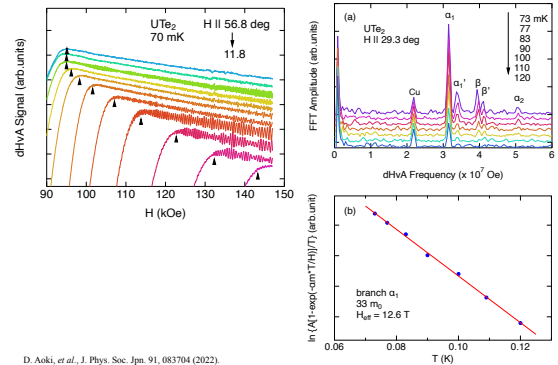
Observation of dHvA oscillations

First Observation of de Haas-van Alphen Effect and Fermi Surfaces in Unconventional Superconductor UTe_2

Dai Aoki^{1*}, Hironori Sakai², Petr Opletal², Yoshifumi Tokiwa², Jun Ishizuka³, Youichi Yanase⁴, Hisatomo Harima⁵, Ai Nakamura⁶, Dexin Li¹, Yoshiya Homma¹, Yusui Shimizu¹, Georg Knebel⁶, Jacques Flouquet⁶, and Yoshinori Haga²

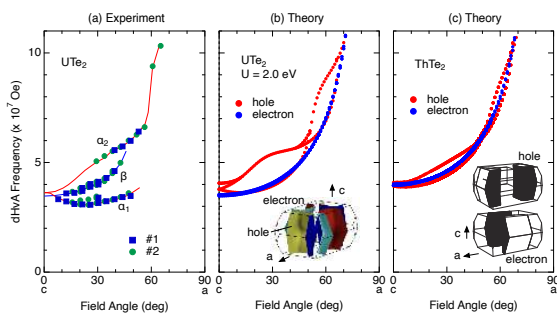


Observation of dHvA oscillations



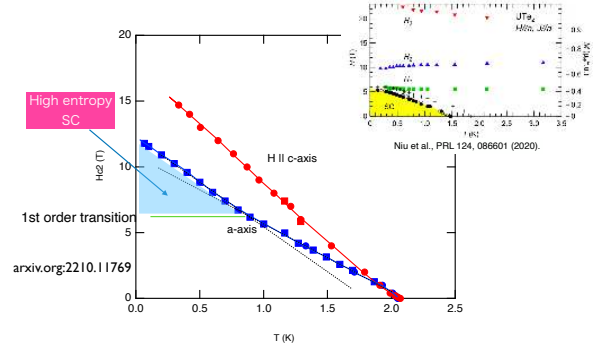
D. Aoki, et al., J. Phys. Soc. Jpn. 91, 083704 (2022).

Observation of dHvA oscillations



D. Aoki, et al., J. Phys. Soc. Jpn. 91, 083704 (2022).

More anomalies in pure samples



$H_{c2} \parallel a$ significantly larger than standard samples (typically $6T = \text{Lifshitz ?}$)
Above $6T$ slope increases

Summary

- UTe_2 :
- Sample-dependent physical properties arising from uranium deficiency.
 - High-quality crystal growth from molten salt
 - clarifying intrinsic properties
 - no residual electronic density of state ($T \rightarrow 0$)
 - Quantum oscillations detected: Fermi surface
 - Multiple superconducting phases

Question and answer session

Q: Are the defects related to the valence and oxidation number of uranium intrinsic to the superconducting properties of the present case? Is this phenomenon happen by chance in a compound with tellurium?

A: It happened by chance (with tellurium), but it is still definitely because it is uranium. There are too many unusual superconductors in uranium. It is important to make it work by using the flexibility of uranium's valence in combination with tellurium. But it is very difficult to understand precisely.

Q: Was the molten salt suitable for growing high purity crystals by was the purity of the molten salt considerably high? Or are there no impurities in the molten salt for crystal growth?

A: We have not experimentally determined the amount of trace impurities. However, X-ray diffraction and compositional analysis have so far found no impurities other than uranotellurium. One of the reasons for our success with molten salt is the reducing atmosphere.

Q: Did you start out by mixing that uranium and tellurium in a single substance and then molten it?

A: That is correct. The key is the initial composition ratio, starting with a uranium-rich stoichiometric ratio.

Q: How do you know the uranium valence experimentally?

A: I would love to know. In this UTe_2 , the formal valence of U is tetravalent because it is componentometric in the Fermi surface. The only way to determine the valence experimentally is to look at the ion size, i.e., the structural parameters.

2.4 M. Nakase (Tokyo Inst. Tech.)

On a New Approach to Exploration of Novel Solvent Extraction Systems for Minor Actinide Extraction for Next Generation Reprocessing

2023.3.02-03@Kumatori

“Users meeting on Condensed-matter Chemistry in Actinides and their Applications / Production of medical RIs by Reactor Irradiation

On a New Approach to Exploration of Novel Solvent Extraction Systems for Minor Actinide Extraction for Next Generation Reprocessing

Tokyo Institute of Technology, Institute of Innovative Research, Fukushima Reconstruction and Revitalization Research Unit
Masahiko Nakase (Ph.D.)

Background

2

- To realize a Zero-Carbon society by 2050, nuclear energy utilization is essential
- Problems related to **nuclear waste** should be solved, and **reprocessing** is one of the keys
- Higher-burnup spent fuels and MOX spent fuels require **MA partitioning** for final disposal
- ⇒ Evaluation of the entire fuel cycle (scenario study) is needed

Tokyo Tech and JAEA developed an integrated nuclear fuel cycle simulator; "NMB4.0." which is available for free!

VISIT HERE!
<https://nmb-code.jp/english>

Background

Current status of MA partitioning

- Separation of trivalent RE and MA is difficult in highly acidic conditions (Am^{3+}/RE^{3+})
- Safety of the next generation of reprocessing plants should be enhanced
- ⇒ The current hydrocarbon diluent, such as *n*-dodecane, has a **flash point** and is **flammable**.
- The **solubility of MA extractants** into hydrocarbon diluent is not high, and the **third phase can be formed**.

Hydrofluorocarbon (HFC)

- Some of the Hydrofluorocarbon(HFC) and Hydrofluoroolefin (HFO) have **no flash point**, **no toxicity**, **low ODP** and **inherently safe**
- Applicability to solvent extraction as diluent is already proved.
- Chemical properties can be tuned by the structural modification

	Vertrel XF	SF33	SF10
Boiling point	55	33	110
Thermal stability	Excellent	good	Good
Latent heat of vaporization [kJ/kg]	28.4	166	35.2
Permittivity [ε]	55	33	110
Solubility to water [ppm]	140	7.8×10^2	
Ozone Depletion Potential	0	0	0
Global Warming Potential	1650	2.0	<10

- Which diluent (structure) is suitable?
- Are there any special diluents that can solve the problem of MA extractants? (solubility, 3rd phase)
- How can we efficiently find the candidate?

3

Machine Learning for solvent exploration

Cheminformatics

Chemistry Informatics

Conventional Method

- Material exploration requires **strategic, systematic, and iterative** experiments (and calculation)
- Preparation of various kinds of diluents and extractants is **expensive**
- RI experiments generate **radioactive waste**

Introduction of Machine Learning

- Efficient experiment becomes possible through many schemes; Quantitative Structure-Property Relationships (QSPR) modeling, **experimental design, active learning, transfer learning**, etc...
- Machine learning can help understand the **correlation of factors** and **which factor is essential**
- Machine learning is effective when the experiments are **complex and expensive**.

Machine Learning is compatible with nuclear chemistry!

4

Approach and Goal

5

Goal; Develop the prediction scheme and find an excellent diluent for MA separation.

Experiments

Thermodynamic data(ΔE), chemical properties (solubility, permittivity, density, viscosity, reflectivity, water contents, etc.), complex structure, aggregation

Chemical calculation

Design virtual molecules

Calculation of chemical properties; COSMO Therm, HSPIP software

Solvent Effect, Anionic effect

First principle molecular dynamics calculation

Mechanistic studies

Application

- Inverse modeling; candidate solvents
- Engineering and applicability; Safety, process design, radiation resistance, waste, regulation etc

Implementation

Solubility

100 mmol/L T2EH-DGA

C3 C4 C5 C6 C7 C8

- F-solvent with small molecule size is better for solubility
- Extractant(DGA) with shorter chain length seems to be better for F-solvent

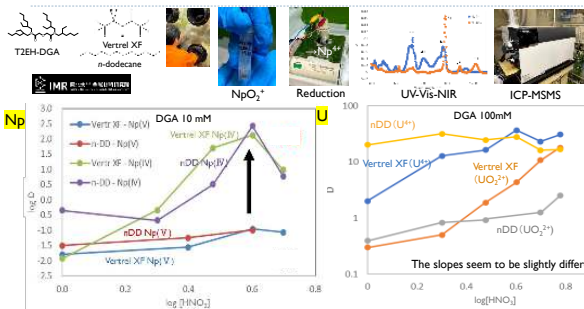
6

Multiple Regression of %E of Am from SMILES

13

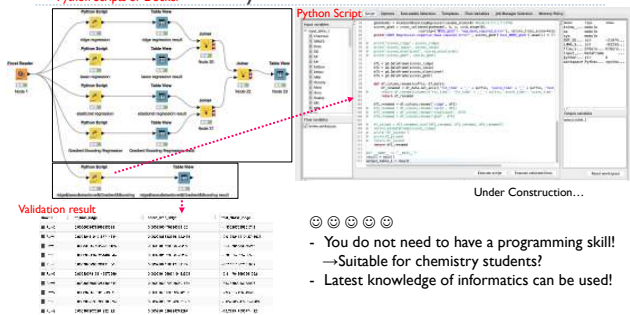
To be reported

Effect of solvents on extraction behavior of Actinide – Np, U



14

Python to KNIME



Conclusion and future perspective

16

- Cheminformatics scheme is applied to the exploration of diluents for MA partitioning
- Regression study was implemented by excel, HSP17, Python, and KNIME.
- Simple regression was not successful as we expected, but multiple regression was successful.

- Upgrade the ML models and KNIME workflow
- Inverse modeling and confirm by MA extraction
- Understand the further mechanism of solvent effects and related phenomena.
- Apply advanced techniques of Machine Learning, such as **transfer learning**

Acknowledgement

17

Actinide experiments
Laboratory for alpha-ray emitters, Tohoku Univ.
Qarai center, Tohoku Univ.
- Dr. K. Shirasaki and Dr. Li Dixin, Mrs C. Abe

Fund
- MEXT Innovative Nuclear Research and Development Program Grant Number JPMXD0221459189 (for younger scientists).
- Internal fund of Mitsubishi Heavy Industries

名古屋大学
NAGOYA UNIVERSITY
Program Advisor
Dr. Kota Matsui

+ Programmer

Question and answer session

Q: In machine learning, there are methods that can be correctly represented for reasons unknown.

A: By using "KNIME," we are trying to create a platform that allows a variety of methods. We want to do everything: visualization tools, statistical processing, etc. We can do the investigation of mechanisms and the exploration of suitable solvents.

Q: Although it is a relatively simple system at the moment, there are methods to include the results of first-principles calculations of solids and molecules in machine learning, so that the physical and chemical effects of each parameter can be understood.

A: Yes. We would like to consider such a study. As a result of first-principles calculations, we can discuss the importance of energy, such as HOMO-LUMO, or conversely, the importance of geometry.

Q: Is there a vertical correlation between lanthanides and actinides in the periodic table?

A: They are very similar. However, the wet separation technology is not highly separated, so there is room for improvement.

2.5 A. Ishii (Teikyo Univ. of Science)


New optical functions opened up by rare- earth hybrid materials

Open meeting on Condensed-matter Chemistry in Actinides and their Applications / Production of medical RIs by Reactor Irradiation
March 2nd, 2023
Main Conference Room, Office Building, KURINS, Kyoto University

**希土類ハイブリッド材料が拓く新光機能
New Optical Functions opened up
by Rare-earth Hybrid Materials**

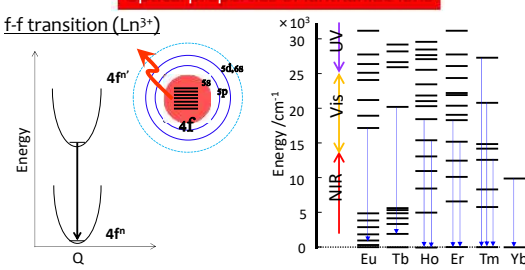
Ayumi ISHII
Teikyo Univ. of Science, JAPAN
E-mail: ayumi-i@ntu.ac.jp

ISHII Lab HP ↓



Optical properties of lanthanide ions

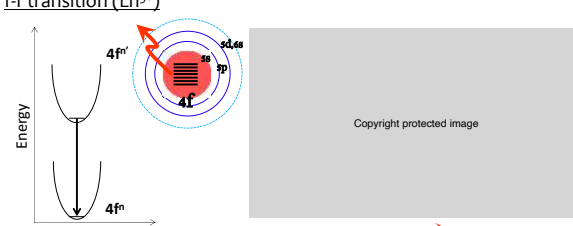
f-f transition (Ln^{3+})



- ★ Inner unoccupied 4f orbitals shielded by occupied 5s and 5p orbitals
⇒ Very sharp emission/absorption bands (UV to NIR)
- ★ Electric dipole forbidden (Laporte forbidden) transition
⇒ Long emission lifetime (~ms), but a poor light absorption coefficient ($\sim 1\text{--}10 \text{ M}^{-1} \text{ cm}^{-1}$)

Optical properties of lanthanide ions

f-f transition (Ln^{3+})



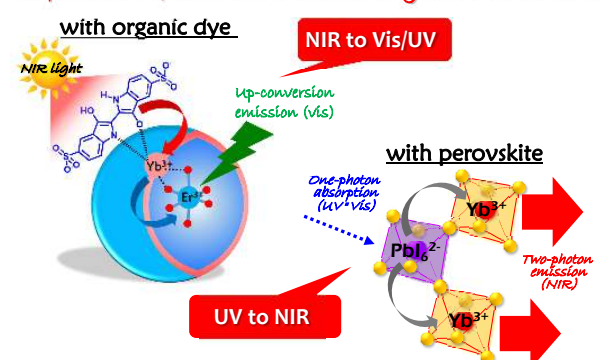
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UV to Vis

To Control NIR light ...
Preparation of Lanthanide-based Hybrid Materials !!

with organic dye **NIR to Vis/UV**

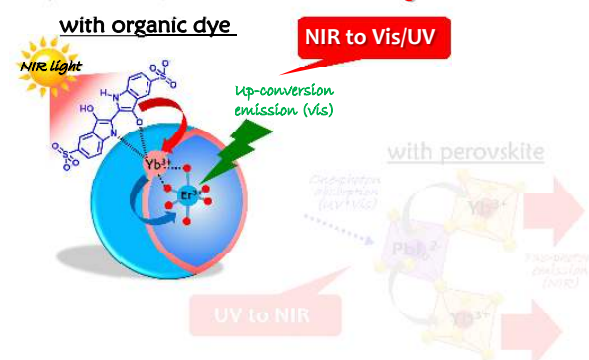
with perovskite **UV to NIR**



To Control NIR light ...
Preparation of Lanthanide-based Hybrid Materials !!

with organic dye **NIR to Vis/UV**

with perovskite **UV to NIR**



Up-Conversion: UC

Donor Acceptor

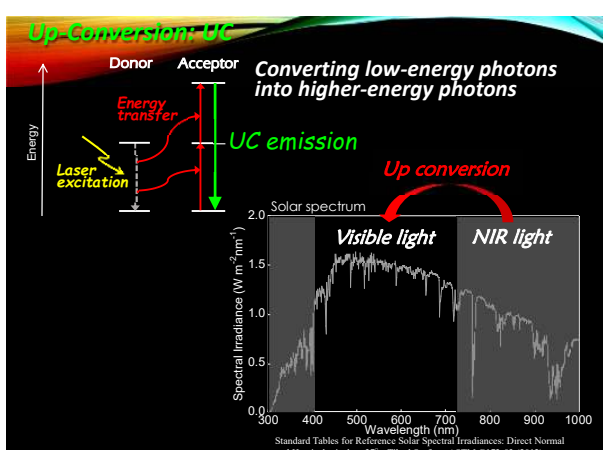
Energy transfer

Laser excitation

UC emission

Up conversion

Converting low-energy photons into higher-energy photons



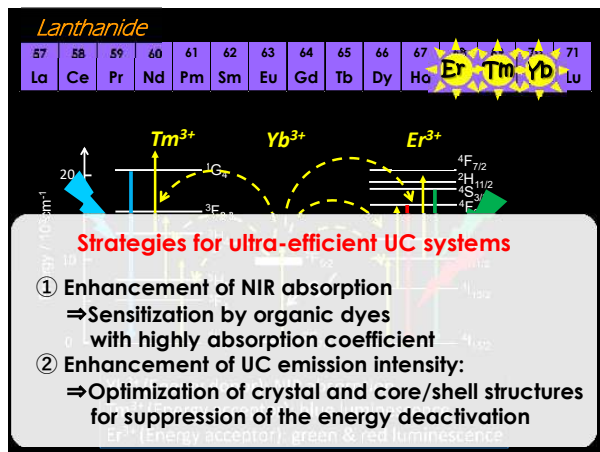
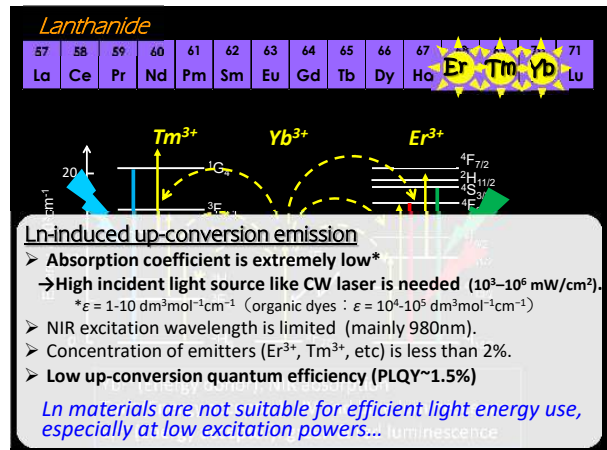
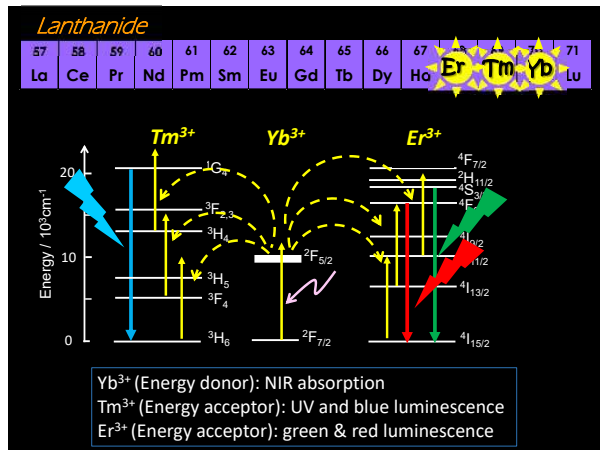
Spectral irradiance ($\text{W m}^{-2} \text{ nm}^{-1}$)

Wavelength (nm)

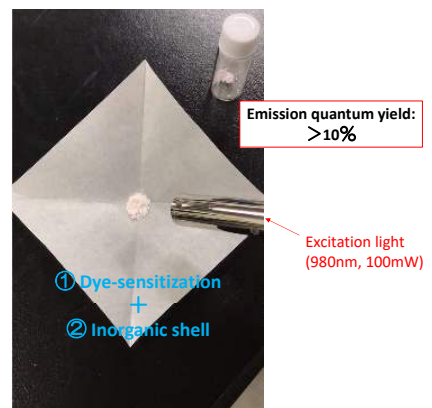
Solar spectrum

Visible light NIR light

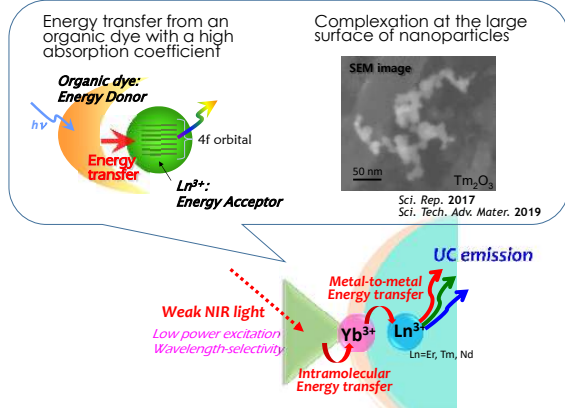
Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface, ASTM G173-03 (2012)



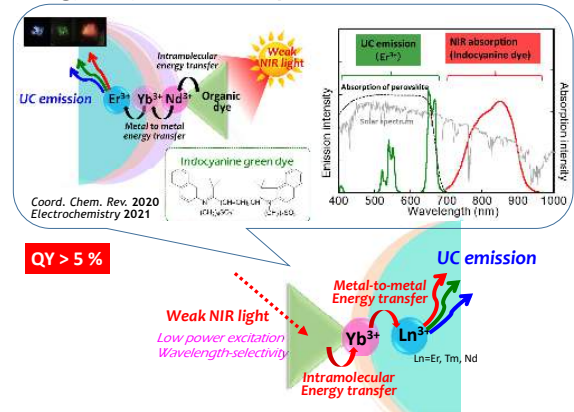
Ultra-efficient UC nanoparticles



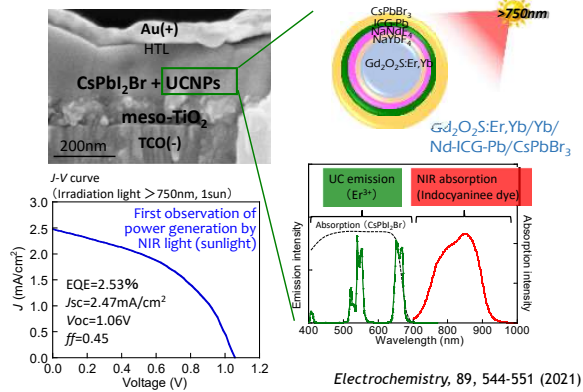
Strategy ①: Dye-sensitized up-conversion



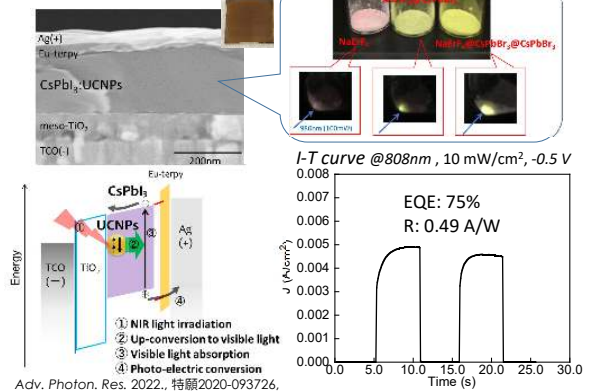
Strategy ①: Dye-sensitized up-conversion



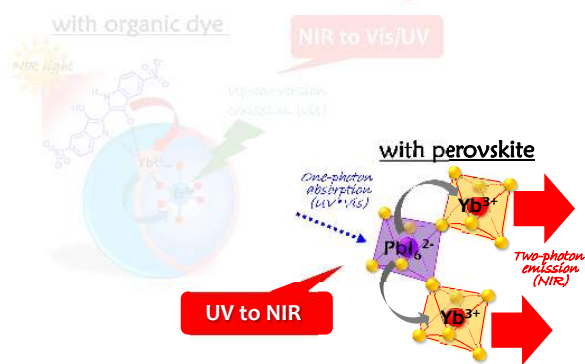
Cf. NIR sensitive perovskite solar cell with dye-sensitized UCNP



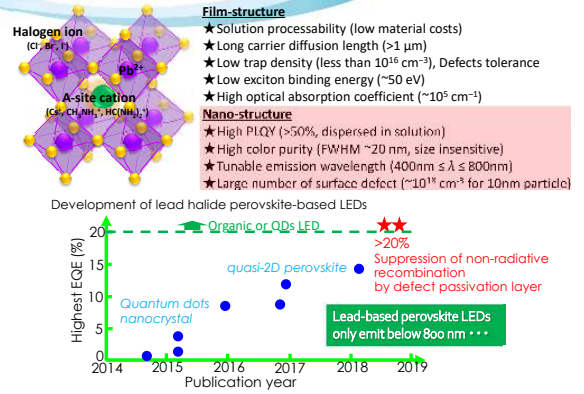
Cf. Up-converting NIR Detection in Lead Halide Perovskite with Core-shell Nanoparticles



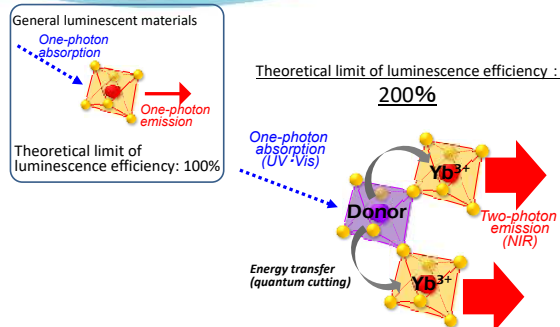
To Control NIR Light ... Preparation of Lanthanide-based Hybrid Materials !!



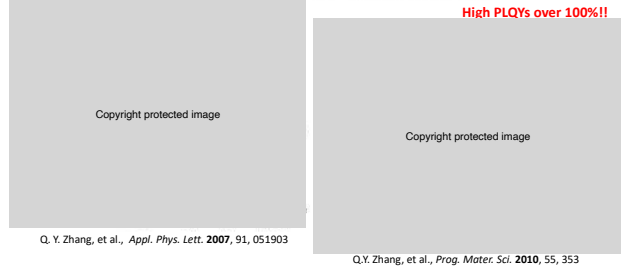
Lead halide perovskites for applications in LEDs ...



Converting one photon (absorption) into two photons (emission) ⇒ NIR emission efficiency higher than 100% (up to 200%).

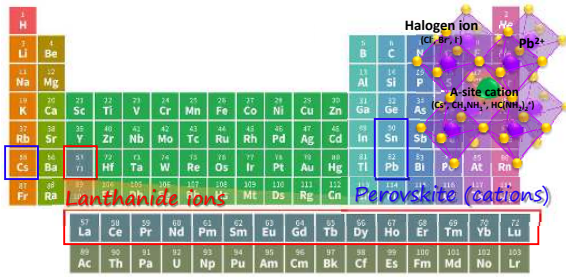


Cf. NIR Quantum-cutting in Ln³⁺-Yb³⁺ (Ln = Pr, Tb, Tm)



Energy donor with UV light absorption is required ...

- △ Lanthanide ion : weak UV light absorption (f-f transition)
- ◎ Lead chloride perovskite (CsPbCl₃): strong UV light absorption



Lanthanide ion (Ln³⁺): CN (coordination number) ≥ 6
 Perovskite: CN = 6 for Pb²⁺ (B-site), CN = 12 for Cs⁺ (A-site)

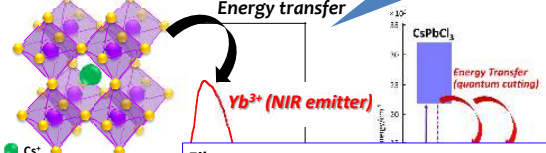
Lanthanide ions are easily doped into the crystal lattice of perovskites (ABX₃)

For highly efficient NIR luminescence of Yb ion ...

Sensitization from perovskite:
Quantum-cutting energy transfer

Application for highly efficient NIR LEDs!!

Perovskite (light absorber)

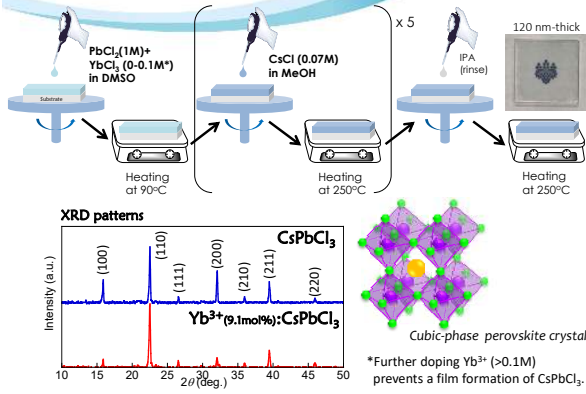


Film-structure

- ★ Solution processability (low material costs)
- ★ Long carrier diffusion length (>1 μm)
- ★ Low trap density (less than 10¹⁵ cm⁻³), Defects tolerance
- ★ Low exciton binding energy (~50 eV)
- ★ High optical absorption coefficient (~10⁵ cm⁻¹)

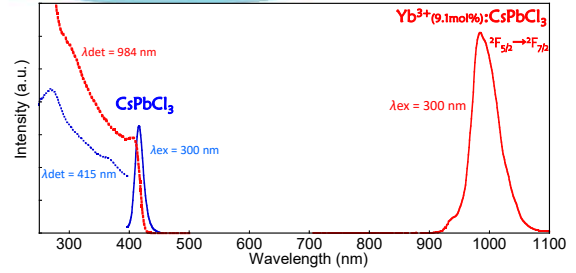
Film formation of Yb³⁺ doped CsPbCl₃ film

Advanced Science, 7, 1903142 (2020)



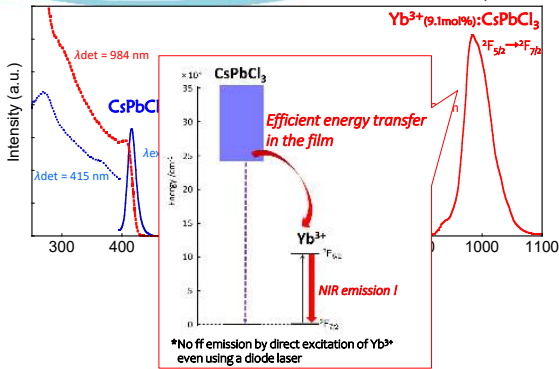
Photoluminescence properties of Yb³⁺ doped CsPbCl₃ film

Photoluminescence (solid line) and the excitation (dotted line) spectra



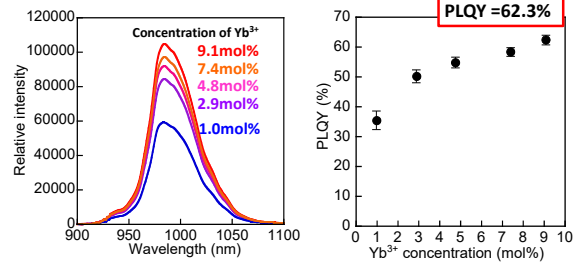
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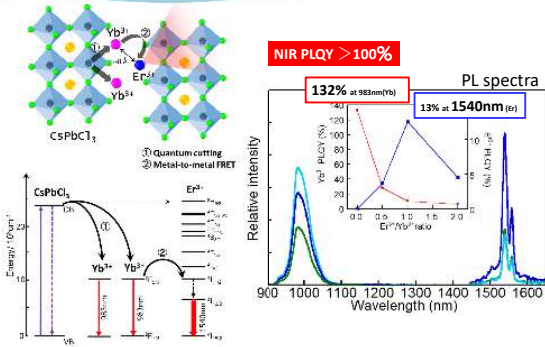
Photoluminescence properties of Yb³⁺ doped CsPbCl₃ film

Concentration dependence of Yb³⁺ on photoluminescence intensity (excitation at 300 nm)



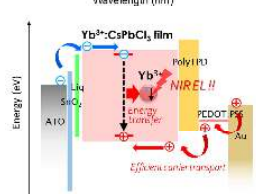
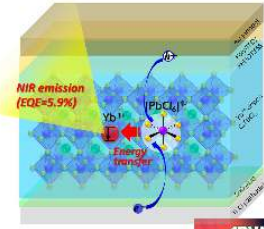
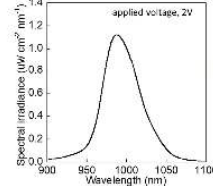
Cf. NIR PLQY over 100% in a layer structured perovskite film

J. Chem. Phys., 153, 194704 (2020)

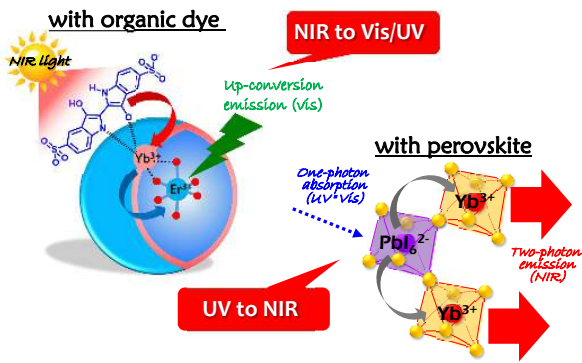


Highly efficient NIR LED based on the quantum cutting energy transfer

Electroluminescence spectrum



**Conclusion :
Lanthanide-based hybrid materials and devices
with new NIR optoelectronic functions**



Question and answer session

Q: Is the matching between the level of the material (dye) with large light absorption and the level of the rare earth important in the compounds emitting rare earth?

A: We focus on energy matching and interface coordination through bond formation.

Q: The upconversion is the process of bringing electrons up to a higher energy level of the rare earths, and during the lifetime of that level, if energy is absorbed again, it can be pumped further up?

A: That is correct. That is why we use levels with long lifetimes.

Q: It seems that the efficiency improves as the size is reduced from nano to micro, but is there any effect of other than particle size?

A: Crystal shape also has a significant effect. In rare-earth transition metals, it is common for the transition probability to drop when the symmetry is high. Crystal lattices with distorted symmetry shine more strongly.

2.6 M. Nogami (Kindai Univ.)

Complexation behavior of actinyl ion- coordinating monoamide compounds with FP ions

Users meeting on Condensed-matter Chemistry in Actinides and their Applications / Production of medical RIs by Reactor Irradiation, KURNS, Kyoto Univ., 2023.3.2

Complexation behavior of actinyl ion-coordinating monoamide compounds With FP ions

Masanobu Nogami

Kindai Univ., Osaka, Japan

Background to develop compounds with selectivity for U(VI) in acidic HNO₃ media

Monoamide compounds in nuclear back-end

- Decrease in generation of secondary wastes would be possible because they consist only of CHON atoms.
- They have a carbonyl oxygen atom which has a strong interaction with actinide (IV) and (VI) species.

Monoamide extractants selectively extract U(VI) and Pu(IV) in acidic HNO₃ media.

Similar adsorptivity is expected for resins.

Monoamide structure: R, R', R'' : hydrocarbon group

Complex of monoamide extractant and U(VI)

Synthesis of silica-supported monoamide resins - 1 step reaction (polymerization) -

Putting silica beads into flask

Evacuation into vacuum

Addition of raw oil (monoamide monomer, DVB, pore producing solvents) into flask

Stepwise polymerization from R.T. up to 90°C in total 15h

Wash of product with acetone (Removal of pore producing solvents)

Wash with water

Resin product

4 kinds of liquid (monomer, etc.)

Porous silica

4 kinds of liquid + silica + initiators

Synthetic scheme

Synthesis of silica-supported monoamide resins - 2 step reaction -

m/p-chloromethylstyrene (CMS) + m/p-DVB

Pore producing solvents

18hr

120°C, 66hr

N-methylacetamide

NaH, DMF

120°C

MVBAA

Synthetic scheme of Silica-MVBAA

Adsorptivity of silica-supported monoamide resins : HNO₃ system (1)

VBAP is non-adsorptive.

K_d values of MVBAA, VBPP, VMAA are low.

Coordination of carbonyl oxygen atoms to U(VI) was difficult, because cyclic structures containing nitrogen atom generates steric hindrance.

Complex of monoamide extractant and U(VI)

DMAA VP MVBAA VBAP VBPP VMAA

[1]M. Nogami, et al., *J. Radioanal. Nucl. Chem.*, 273, 37 (2007).

[2]M. Nogami, et al., *Prog. Nucl. Energy*, 50, 462-465 (2008).

Adsorptivity of silica-supported monoamide resins : HNO₃ system (2)

Chain-type (DMAA) No adsorption of FP ions

Cyclic-type (VP) Adsorption of some FP ions

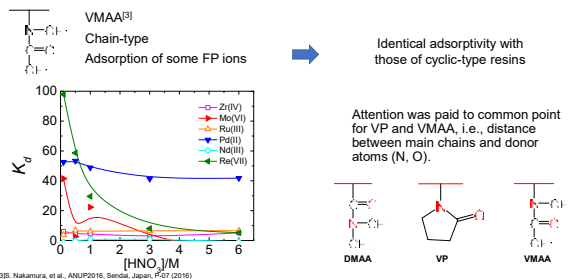
K_d vs [HNO₃]

[1]M. Nogami, et al., *J. Radioanal. Nucl. Chem.*, 273, 37 (2007)

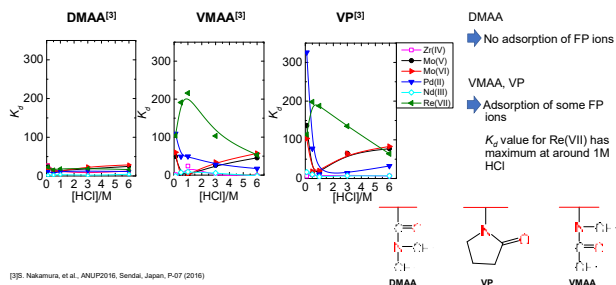
[2]M. Nogami, et al., *Prog. Nucl. Energy*, 50, 462-465 (2008)

[3]S. Nakamura, et al., *ANUP2016*, Sendai, P-07 (2016)

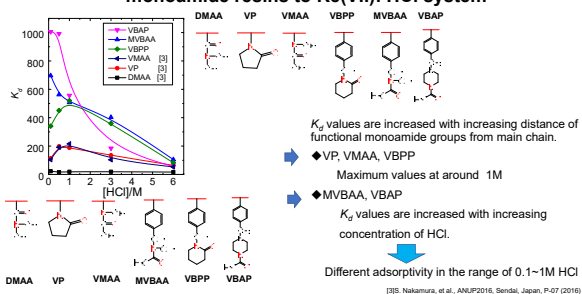
Adsorptivity of silica-supported monoamide resins : HNO₃ system (3)



Adsorptivity of silica-supported monoamide resins to FP ions : HCl system



Adsorptivity of silica-supported monoamide resins to Re(VII): HCl system



Investigation on adsorption mechanism for Re(VII) in HCl system



Chemical species of Re(VII) change with increasing concentration of HCl.

Adsorptivities of various monoamide resins to Re(VII) are found to be different in the range of 0.1~1M HCl.

It is suggested that adsorption mechanism for ReO₄⁻ has significant differences.

Change in chemical forms of Re(VII) depending on HCl concentration^[4]

[4] R. Srivastava, et al., Hydrometallurgy, 157, 33-38 (2015)

Question and answer session

Q: What is the adsorption mechanism?

A: In nitric acid solution, metal ions form complexes and become electrically neutral, similar to liquid extraction. In hydrochloric acid solution, electrostatic interaction is more dominant. Of course, in either aqueous solution system, there are both contributions.

Q: You say you don't have a clear understanding of the role of oxygen and nitrogen in amides. Is there already information, for example, on what kind of behavior would be produced by hanging only carbonyls in a polymer, or tertiary amines?

A: In the nitric acid solution system, the uranyl ion is a hard acid and has a high affinity for oxygen atoms. There have been studies on the use of ketones (C=O) and other compounds that do not contain nitrogen, such as ether bonds (C-O-C), to capture uranium supplements.

Q: Then what is the role of nitrogen?

A: Nitrogen protonates to secondary ammonium in acidic solutions, so we would like to study its effect. With the help of computational chemistry professors, we should have a better understanding.

Q: It was mentioned that the coefficient of extraction is large in a cyclic structure. Since this nitrogen is covered when the ring structure changes, why is there a nitrogen effect?

A: It must be a matter of electron density.

Q: Surely there must be an effect of electron attraction affecting the electron density of oxygen rather than direct coordination.

A: I agree.

Q: If the extractant is loaded on the fixed layer, the extraction rate of elements other than uranium would also increase. What considerations should be made when structuring the separation process?

A: Am I correct in my understanding that, in general, various elements are more likely to be supplemented if they are made solid?

Q: Since there is no diluent, the dilution rate cannot be adjusted.

A: That is correct that there is no diluent. However, the results on the left side of this slide show typical results where only uranium is really supplemented.

Q: But the KD is above 1 for other elements.

A: Yes, but it should be possible to separate them in a chromatographic column. Extraction is difficult.

2.7 K. Shirasaki (IMR, Tohoku Univ.)

Ac-228 solvent extraction by DGA

IMR Users meeting on Condensed-matter Chemistry in Actinides and their Applications / Production of medical PIs by Reactor Irradiation, KURNS, Kyoto University, 2022/02/30

²²⁸Ac solvent extraction by DGA

Institute for Materials Research, Tohoku University
 Kenji Shirasaki, Shingo Sugahara
 Tokyo Institute of Technology
 Masahiko Nakase

Institute for Materials Research, Tohoku University

IMR Contents

1. Background of ²²⁸Ac and Ac solvent extraction by DGA
2. Purpose of this study
3. Experimental
4. Results
 - ✓ Preparation of ²²⁸Ac generator
 - ✓ Solvent extraction by TODGA or T2EHDGA
5. Conclusion

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IMR Targeted alpha therapy (TAT) using ²²⁵Ac

- Actinium chemistry has experienced a strong revival in the past two decades due to the development of a new type of cancer therapy, called "Targeted Alpha Therapy (TAT)"
- One of the isotopes of actinium, ²²⁵Ac, is seen as one of the most promising candidates for targeted alpha therapy
 - ✓ its ideal short half-life of 10 days
 - ✓ decay chain that has no long-lived daughter
 - ✓ delivers 4 high-energy alpha particles, along with two beta particles

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Decay chain of uranium-233 comprising actinium-225 and its daughters.

Dobson G. J. P., et al. The coordination properties and ionic radius of actinium: A 229-year-old enigma. Coordination Chemistry Reviews, 2022,488,224232

Institute for Materials Research, Tohoku University

IMR Circumstances surrounding Actinium

- The main reason for the absence of commercial applications based on actinium (except ²²⁵Ac)...
 - ✓ rare
 - ✓ radioactive
- ²²⁷Ac (t_{1/2} = 21.8 y): longest-lived isotope
 - ✓ present in the environment due to the decay of ²³⁵U
 - ✓ extremely diluted in natural sources
- Hence, actinium materials cannot readily be stockpiled and must be periodically produced in nuclear reactors, cyclotrons, or particle accelerators...

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half-life longer than 1 hour

The sole purpose of studying Ac chemistry is rare, challenging, and extremely costly.

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IMR Chemical properties of Actinium

Dobson G. J. P., et al. The coordination properties and ionic radius of actinium: A 229-year-old enigma. Coordination Chemistry Reviews, 2022,488,224232

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Position of actinium (Z = 89, symbol "Ac") in the periodic table of the elements. For comparison purposes, the adjacent elements belonging to the 6th and 7th rows are highlighted and their preferred oxidation state in aqueous solution is indicated.

The current availability of purified ²²⁷Ac for research in US is below the milligram level.

- The position of actinium in the periodic table also makes it an elusive element since...
 - ✓ the first member of the actinide series
 - ✓ its natural oxidation state in solution is +III
 - ✓ its ion, Ac³⁺, has an empty valence shell (electronic configuration: [Rn] 5f⁰)
- Unlike many other f-element ions (Eu³⁺, Tb³⁺, Dy³⁺, UO₂²⁺, Pu⁴⁺, Cm³⁺...):
 - ✓ spectroscopically silent with no fluorescence properties nor practical absorbance band in the UV-visible - NIR domains
- Bulk chemistry experiments cannot be performed
- Ac³⁺ has no perfect surrogate

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IMR Actinium isotope (²²⁸Ac) advantage

Decay chain (Th series)

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γ-Spectrum from a solution of ²²⁸Ac eluted from the generator

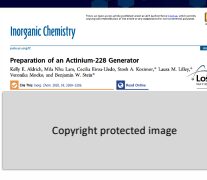
Wolch K.E., et al. Preparation of an Actinium-228 Generator. Inorganic Chemistry, 2002,41,3200-3206

- An actinium isotope (²²⁸Ac, t_{1/2} = 6.15 h):
 - ✓ nuclear properties are well-suited for γ-spectroscopy
 - ✓ easily resolved from the long-lived ²²⁸Th daughter product
 - ✓ rapidly regenerates after being harvested from the ²²⁸Ra (t_{1/2} = 5.75 y) parent

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IMR ²²⁸Ac Generator

The change in ²²⁸Ra and ²²⁸Ac activities vs. time when ²²⁸Ac is routinely "milked" from the ²²⁸Ac generator



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Projected activity of the ²²⁸Ac generator (based on the parent ²²⁸Ra activity)

- ❖ The ²²⁸Ac generator provides frequent and long-term access (of many years) to the spectroscopically "friendly" ²²⁸Ac radionuclide
- ❖ The ²²⁸Ac product can be routinely "milked" from the generator on a daily basis, in chemically pure form, with high specific activity and in excellent yield (~95%)


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IMR Separation of Actinium

❖ DGA extraction chromatography



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- ❖ Load and wash conditions:
 - ✓ ≥90% of Ra²⁺ and ≥80% of Ba²⁺ elute, while Ac³⁺ and Ln³⁺ are quantitatively retained
 - ✓ Residual Ra²⁺ and Ba²⁺ were further removed with 4 M HNO₃
- ❖ The addition of 10 M nitric acid:
 - ✓ More than 99% of the retained Ac is eluted
 - ✓ Ln³⁺ could be eluted with 0.1 M nitric acid
- ❖ Development of DGA resin, which offers a possibility for rapid, robust, and effective separation of Ac from Ra, is key in these techniques


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IMR Diglycolamide (DGA) extractants


❖ In past two decades, diglycolamides have received particular attention of separation groups engaged in the area of actinide partitioning, as these ligands display high affinity for trivalent metal ions as compared to hexavalent metal ions



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IMR Purpose of this study


To demonstrate the usefulness of ²²⁸Ac...

- ❖ Preparation of ²²⁸Ac generator based on previous study and evaluation of ²²⁸Ra yield
- ❖ ²²⁸Ac solvent extraction by two DGA extractants (TODGA and T2EHDGA) for fundamental investigation of actinium coordination chemistry

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IMR ²²⁸Ac generator preparation process

Four-step separation process developed for isolating ²²⁸Ra as a generator for ²²⁸Ac from natural ²³²Th



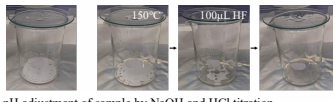
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- ❖ Step 1 removes the vast majority of ²³²Th from ²²⁸Ra by hydroxide precipitation
- ❖ Step 2 removes the contaminants originated from ²³²Th starting material and bulk Na⁺ introduced from NaOH
- ❖ Step 3 separates ²²⁸Ra from its daughters, including ²²⁸Ac and ²¹²Pb, and trace-level impurities
- ❖ Step 4 separates organic impurities by filter

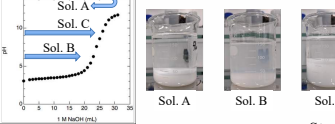
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IMR Generator preparation process(step1)

ThO₂ dissolution in conc. HCl



Sol. A ← Sol. C ← Sol. B



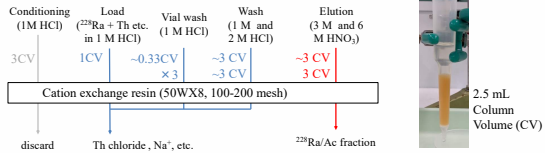
- ❖ Stock sol. (Th⁴⁺ in 0.1 M HCl):
 - ✓ ThO₂ dissolution in HCl
 - ✓ addition of catalytic amount of HF
- ❖ Th hydroxide precipitation
 - ✓ NaOH (30 wt%) is added to adjust the pH >8
 - ✓ voluminous pasty-white solid
 - ✓ the pH of the basic slurry is adjusted to 6 < pH < 8 with HCl
 - ✓ filtrate and adjust HCl to 1M

Step1: <5.1 ppm Th, 100% ²²⁸Ra remain

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Generator preparation process(step2)

❖ Cation exchange chromatography



❖ Load and wash conditions:

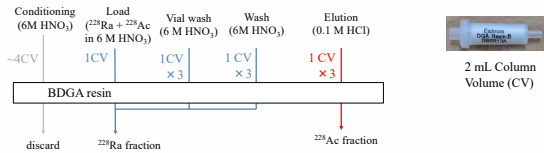
- ✓ Ra²⁺ and Ac³⁺ are retained
- ✓ Neutral complexes, anions, and the majority of the Na⁺ pass through the column
- ❖ Ra²⁺ and Ac³⁺ products are then eluted with HNO₃ and are isolated

Step2: 97% ²²⁸Ra remain

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Generator preparation process(step3)

❖ DGA extraction chromatography



❖ Load and wash conditions:

- ✓ Ac³⁺ are retained
- ✓ The majority of the Ra²⁺ pass through the column
- ❖ Ac³⁺ products is then eluted with HCl and is isolated

Step3: ~100% ²²⁸Ra remain

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Summary of ²²⁸Ac generator preparation

Table ²²⁸Ra separation percentage in each steps

	Step1	Step2	Step3	Total
Aldrich et al.*	83 %	98 %	100 %	81 %
This work	100 %	97 %	97 %	94 %

*Fukuda et al., Preparation of an Actinium-228 Generator, Inorganic Chemistry, 2020, 59, 3200-3208

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❖ The ²²⁸Ac generator:

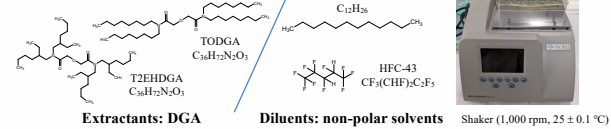
- ✓ isolating the ²²⁸Ra parent and operating the generator do not require the addition of carrier
- ✓ chemically pure and high specific activity
- ✓ small volumes of dilute acid, which will facilitate matrix manipulation of the product for subsequent experiments
- ✓ a long shelf life which can provide access to large quantities of ²²⁸Ac for many years

ca. 0.34 kBq ²²⁸Ra separated

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Tests of ²²⁸Ac solvent extractions

❖ Chemicals, apparatus and procedure



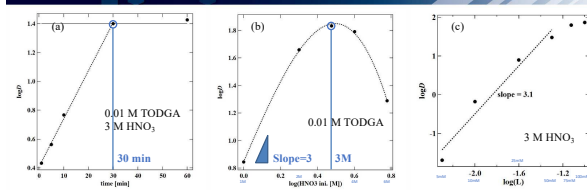
- ✓ Separation and purification of ²²⁸Ac from ²²⁸Ac generator and adding to the aqueous phase
- ✓ it is mixed with the organic phase containing DGA and started shaking
- ✓ Stop after, aliquot of the aqueous phase is sampled and measured γ -ray spectrum using Ge semiconductor detector

Shaker (1,000 rpm, 25 ± 0.1 °C)

Ge semiconductor detector

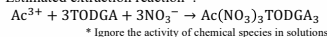
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²²⁸Ac extraction behavior by TODGA



Dependence of shaking time (a), nitric acid concentration (b) and TODGA concentration (c) using n-dodecane as diluent.

❖ Estimated extraction reaction*:



* Ignore the activity of chemical species in solutions

❖ Same behavior observed in Lns and Am³⁺ extractions*:

*Sasaki et al., An Additional Insight into the Correlation between the Distribution Ratio and the Apparent Acidity of the TODGA System, IJER, 2002, 21, 247-254

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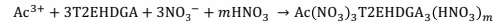
²²⁸Ac extraction behavior by T2EHDGA



❖ Estimated extraction reaction:

- ✓ different from TODGA condition in terms with acid molecule extraction
- ✓ Diluent effect is clearly indicated in acid concentration dependence

❖ Estimated extraction reaction*:



* Ignore the activity of chemical species in solutions

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IMR Ans and Lns extraction by DGA



Distribution of lanthanides and actinides by 0.01 M T2EHDGA dissolved in HFC-43.



Distribution of lanthanides and actinides by 0.1 M TODGA dissolved in n-dodecane from 1 M HNO₃.

❖ Series extraction behavior:

- ✓ Similar tendency can be observed both T2EHDGA and TODGA
- ✓ Main factor of difference between Ans and Lns is still unclear...extractant or diluent effect?

IMR Summary of ²²⁸Ac solvent extraction by DGA

❖ Extraction mechanism seems to be strongly dependent to side chain of DGA motely:

Estimated extraction reaction*: * Ignore the activity of chemical species in solutions



✓ $m = 0$ for TODGA, 2 or 4 for T2EHDGA

✓ In T2EHDGA condition, diluent effect is clearly indicated in acid concentration dependence ($m = 2$ for HFC-43 and 4 for n-dodecane)

❖ Lns and Ans series extraction behavior shows similar tendency between T2EHDGA and TODGA conditions

IMR Conclusion

Good demonstration the usefulness of ²²⁸Ac

- ❖ Quantitative purification of ²²⁸Ac was possible, reproducing results from the previous study
 - ✓ ²²⁸Ra yield is 94% in total process
- ❖ The difference of ²²⁸Ac solvent extraction by two DGA extractants (TODGA and T2EHDGA) provides some insights
 - ✓ Extraction mechanism seems to be strongly dependent to side chain of DGA motely
 - ✓ Lns and Ans series extraction behavior shows same tendency in two DGA extractants

Thank you for your attention

Question and answer session

Q: In the process of producing actinium-228, you say that thorium precipitated perfectly with pH adjustment, what do you do when you extract it from thorium again?

A: Precipitate it in the form of hydroxide, dry the hydroxide and store it in solid form, and dissolve it again in nitric or hydrochloric acid. Radium-228 can be recovered relatively easily this way.

Q: Isn't the accumulation of solid alpha waste of metal nitrates and chlorides a problem?

A: That is correct and is an improvement of this method.

Q: Why was actinium deviated from the straight line in the last figure (comparing the extraction capacity of the actinide and lanthanide series in terms of distribution ratio)? Is it due to the mass effect of actinium or the lack of f orbital electrons in the actinium ions?

A: In the case of TODGA, the actinium extraction experiment has not yet been completed, and we believe that it will probably ride on the straight line. However, the reason why the distribution ratios of the actinide and lanthanide series are reversed in TODGA and T2EHDGA is currently unknown, and we would like to clarify whether this is due to the diluent (HFC and dodecane) or the structure of the extractant DGA.

2.8 T. Kobayashi (SPring-8, JAEA)

Achievements in the facility utilization of the Combined Research Laboratory and the current status with the SPring-8 JAEA Harima Lab.

Users meeting on Condensed-matter Chemistry in Actinides and their Applications/
Production of medical RIs by Reactor Irradiation / Mar. 2023

Achievements in the facility utilization of the Combined Research Laboratory and the current status with the SPring-8 JAEA Harima Lab.

**複合研の施設供用での成果と
SPring-8 JAEA播磨ラボとの現状について**

Tohru Kobayashi, Tsuyoshi Yita
Materials Sciences Research Center, JAEA

小林 徹、矢板 毅
日本原子力研究開発機構
物質科学研究センター

共同利用の成果 —模擬デブリの性状変化に関する研究—

福島第一原子力発電所の事故によって発生した燃料デブリの化学状態や経年変化、デブリ取り出し時に予想される環境変化に伴う性状変化を明らかにする。

模擬した試料を作成
放射光XAFS分析

浸水してγ線照射した
模擬デブリ試料

Spring-8 BL22XU
(JAEA専用ビームライン)
XAFS測定装置

事故後の1F原子炉の模式図

LINACでγ線照射

研究内容

【模擬した条件】

- ・燃料と構造体の溶融物
- ・浸水状態
- ・高放射線場
- ・デブリ取り出し時の雰囲気変化

→

- ・UとZrを焼結した試料を作成 (JAEA東海)
- ・ペレットを水に浸す
- ・γ線を照射 (京大複合研 LINAC)
- ・ペレットを大気に晒す

↓

・XAFSを測定 (JAEA播磨ラボ)

【実験の概要】

U_{0.7}Zr_{0.3}O₂焼結体 浸水してγ線照射 浸水し続ける 大気に晒す

試料調製

①試料を石英セルに封入

②水を入れたステンレス缶に試料を設置。

ステンレス缶を設置

Ptターゲット

ブローワーで缶を空冷

③ステンレス缶を設置して照射

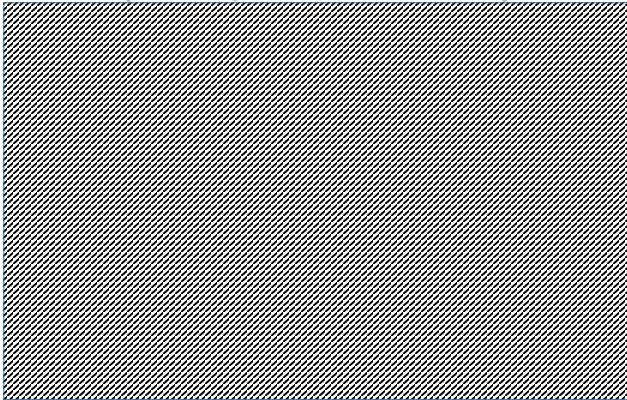
・1kGy/hで60時間照射

TLDで照射線量を評価

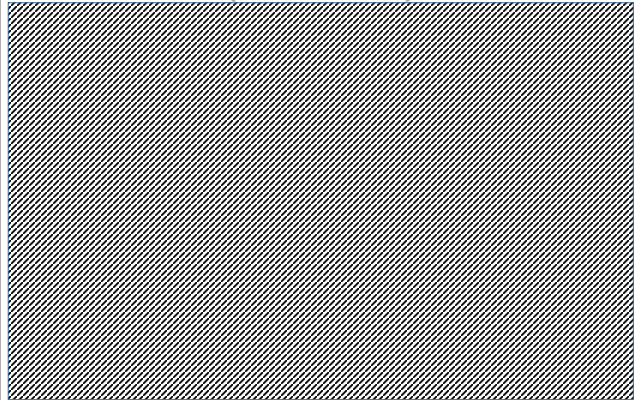
γ線照射した模擬デブリのXANESスペクトル① (長時間浸水、蛍光法にて測定)

γ線照射した模擬デブリのXANESスペクトル② (γ線を再照射、蛍光法にて測定)

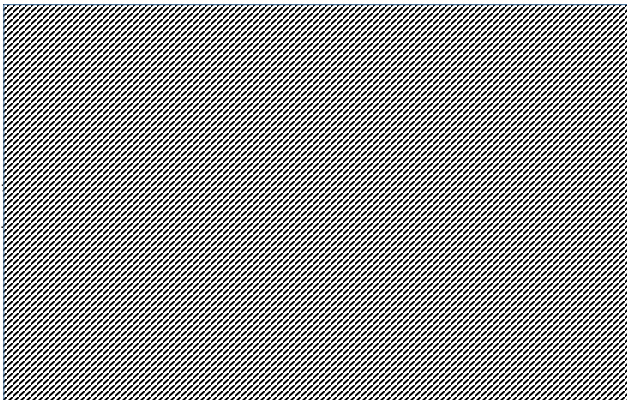
**γ線照射した模擬デブリのXANESスペクトル③
(浸水せずγ線照射、蛍光法にて測定)**



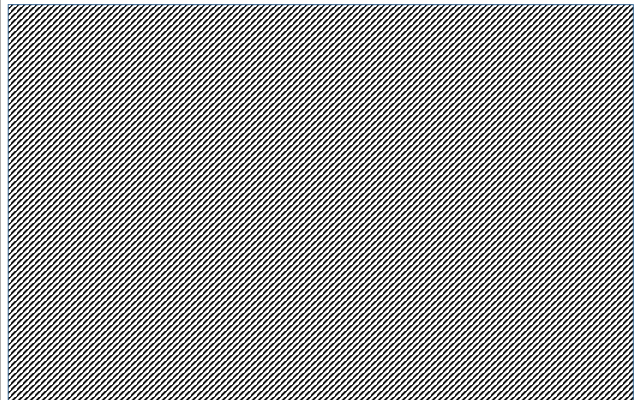
**浸水した上澄み液のXANESスペクトル
(蛍光法にて測定)**



蛍光法と透過法の比較



模擬デブリ中のウランの化学状態変化



JAEA 物質科学研究センター

中性子および放射光を利用した物質科学研究の推進

放射光エネルギー材料研究ディビジョン
〔播磨地区〕

SPring-8で2本の専用ビームラインを運営



中性子材料解析研究ディビジョン
〔東海地区〕

試験研究炉JRR-3で12台の装置を運営



定常中性子線

JAEAの第4期中長期計画(R4~R10年度)での位置付け

□ JRR-3等の定常中性子源の特徴を活かした中性子利用技術及びSPring-8等の特徴を活かした放射光利用技術を進展させ、ハルス中性子との相補的・相乗的利用も推進し、先端機能性材料・エネルギー材料の開発・機構解明や社会インフラ基盤評価、アクチノイド基礎科学及び分離等のための基礎概念の構築、廃炉・廃棄物処理に資する研究開発等、基礎から応用まで幅広い研究・技術開発を行い、持続可能な社会の実現に貢献する。



ハルス中性子線

JAEA SPring-8におけるJAEAビームラインと設置装置

エネルギー分散型XAFS装置 (DAPF) BL14B1 (cst専用BL) 硬X線と軟X線を使い分けた物性評価

RI実験棟 ミクロ構造 + 電子状態

蓄積リング線 BL235U (JAEA専用BL) 軟X線

RI実験棟 高圧分光電子分光装置 (LAPPER) 軟X線

BL22XU (JAEA専用BL) 硬X線

高圧分光電子分光装置 (LAPPER) XAFS装置 (可変型XAFS) 応用イメージング装置 かつりばい多相解析

高圧分光電子分光装置 (LAPPER) XAFS装置 (可変型XAFS) 応用イメージング装置 かつりばい多相解析

高圧分光電子分光装置 (LAPPER) XAFS装置 (可変型XAFS) 応用イメージング装置 かつりばい多相解析

高圧分光電子分光装置 (LAPPER) XAFS装置 (可変型XAFS) 応用イメージング装置 かつりばい多相解析

Question and answer session

Q: You showed data that oxidation progressed due to gamma irradiation and water immersion; XPS should also show the bulk distribution. Is the depth profile known?

A: This experiment is XAFS, not photoelectron spectroscopy. Depth profile is considered important.

A: No, it is not. Unlike fluorescence, absorption data includes information from the surface to the bulk.

Q: Isn't it important to know how deep the oxide film is formed on the surface?

A: That is exactly right. At this time, we only have information that reflects a large amount of the surface and a large amount of the bulk, and this is all we know. In the future, we would like to examine the extent to which oxidation has progressed on the surface through experiments such as angular resolution.

Q: Isn't it time to start accepting debris?

A: We will be able to report that we have measured the actual debris as early as next fiscal year. Currently, we are working on establishing various operational systems.

2.9 Y. Kasamatsu (Osaka Univ.)

Recent chemical researches on nobelium

重アクチノイド、 ノーベリウムの化学研究 (Recent chemical researches on nobelium)

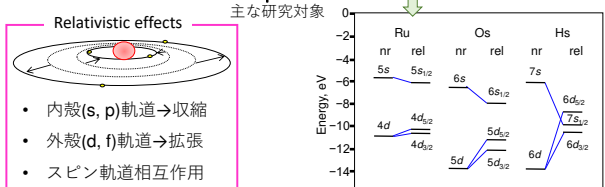
Graduate School of Science,
Osaka Univ.
Yoshitaka KASAMATSU

Heavy element chemistry

周期表の最下段 第7周期元素の化学

原子番号 $Z > 100$ (Heavy elements)
全て人工合成、人類にとっての**新元素**!

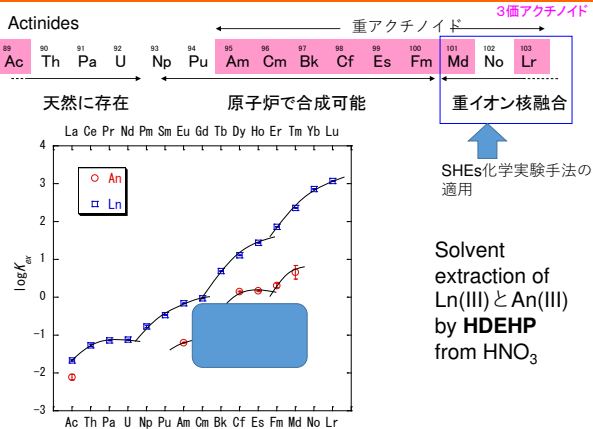
H	He																	Hs														
Li	Be																	Uu														
Na	Mg																	Nh														
K	Ca																	Uuq														
Rb	Sr																	Uub														
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hf	Hs	Mt	Ds	Rg	Cn	Ni	Fl	Mc	Lv	Ts	Og



相対論効果が重元素の化学的性質に影響 ⇒ 特徴的な化学的性質 (実験)
元素の理解 ← 相対論の理解 ← 相対論計算 ←

Actinide element chemistry

アルファ研究会
2015.2.23



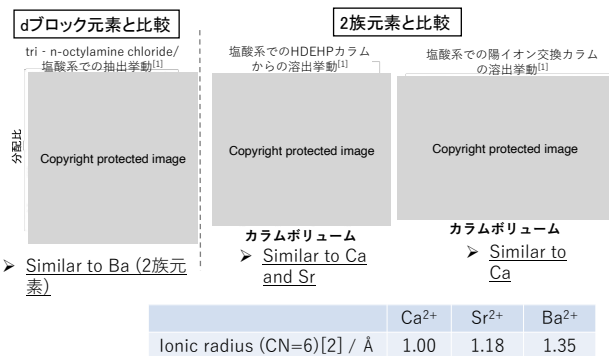
Nobelium (No)

- Atomic number = 102, Heavy element
- In f-block elements, only No stably has +2 state in aq, while all lanthanides and heavy actinides have +3

H	He																	Hs														
Li	Be																	Uu														
Na	Mg																	Nh														
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr															
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe															
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hf	Hs	Mt	Ds	Rg	Cn	Ni	Fl	Mc	Lv	Ts	Og
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																		
+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3																
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																		
+3	+4	+5	+6	+5	+4	+3	+3	+3	+3	+3	+3	+3	+2	+3																		

Stable oxidation state in aqueous solutions

Nobelium (No)



塩酸系ではなく2族元素と錯形成をする系でNoの性質を調べたい

[1] R. J. Silva, et al., Inorg. Chem. 13, 2233 (1974).

[2] R. D. Shannon, Acta Cryst. 32, 751 (1976).

Recent researches on No

Co-precipitation method

- Co-precipitation with samarium hydroxide
- **Co-precipitation with barium sulfate**
- Co-precipitation with calcium oxalate
- Co-precipitation as malonate

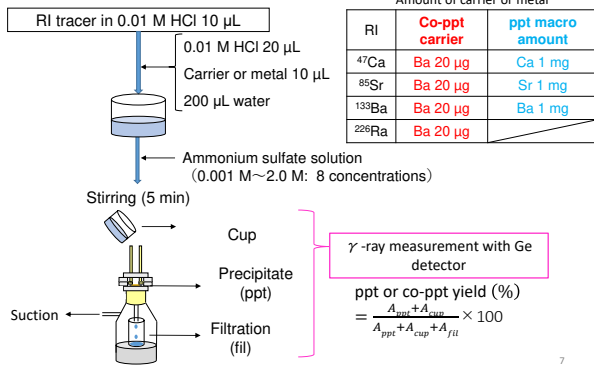
Solid-liquid extraction

- Extraction by crown ether resin
- アームドクラウンエーテル樹脂

Precipitation and Co-ppt- as sulfate

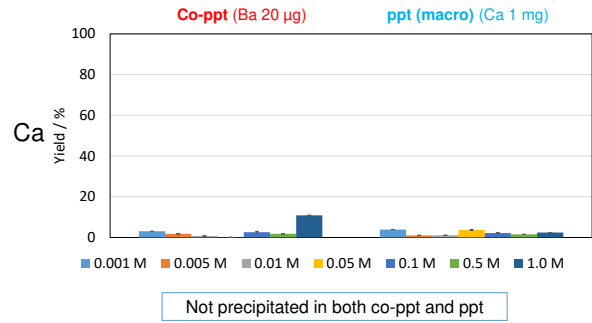
Experiment

⁴⁷Ca: Produced by neutron irradiation at KURNS
⁸⁵Sr, ¹³³Ba: Produced by proton irradiation at RCNP



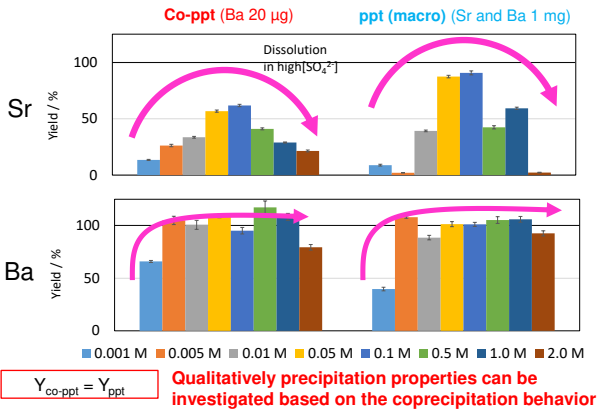
7

Precipitation and Co-ppt- as sulfate



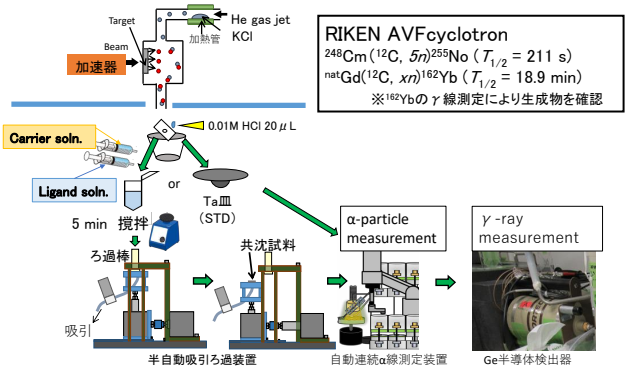
8

Precipitation and Co-ppt- as sulfate



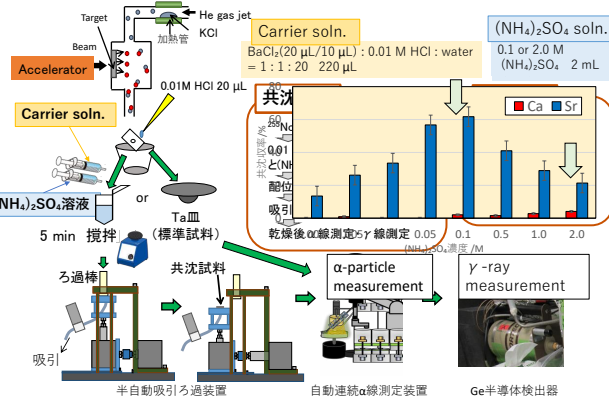
9

Online experiment of ²⁵⁵No



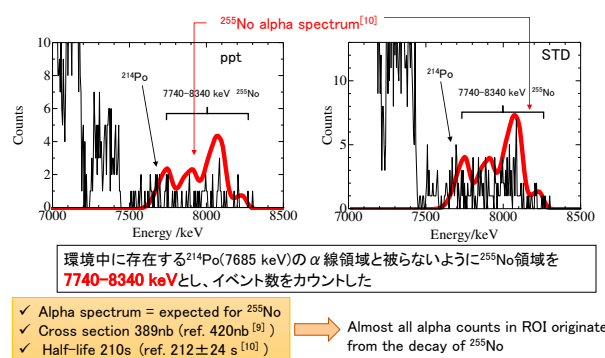
10

Online experiment of ²⁵⁵No



11

Results and discussion ²⁵⁵No



[9] T.Sikkeland et al., Phys. Rev. 172, 1232 (1968). [10] M. Asai et al., Phys. Rev. C. 83, 014315 (2011).

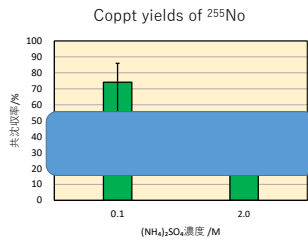
12

Results and discussion ²⁵⁵No

各条件ごとに数えた²⁵⁵Noのカウンtr数
それぞれ²⁵⁵No捕集終了時の計数率(cps)
に直し共沈収率を求めた

Correction for

- Half-life
- Yield (compared with Yb)
- Evaporation yield
- Beam current
- Detection efficiency
- Background of alpha counts
- Tailing of α spectrum

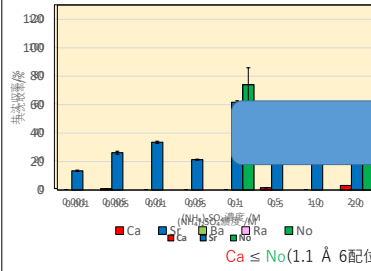


$$\text{Cociprecipitation yield / \%} = \frac{\text{Count rate of co-ppt (cps)}}{\text{Count rate of STD (cps)}} \times 100$$

(NH ₄) ₂ SO ₄ 濃度 / M	0.1 M	2.0 M
Yield/%	74.09	41.80
error(+)	11.85	6.69
error(-)	23.87	15.66

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Results and discussion ²⁵⁵No



硫酸沈殿の性質^[11]

SO₄²⁻ (2.44 Å) と2族元素のイオン半径差が小さいほど水和しにくくなり、沈殿を形成する

硫酸錯体の溶解度積^[12]とイオン半径^[13]

	溶解度積 (logK _{sp})	M ²⁺ Ionic radius (CN=6)/Å
CaSO ₄	-4.63	1.00 (6配位)
SrSO ₄	-6.53	1.18 (6配位)
BaSO ₄	-10.00	1.35 (6配位)
RaSO ₄	-14.38	1.48 (6配位)

Ca ≤ No (1.1 Å 6配位) < Sr

Previous works

- Between Ca and Sr
- Similar to Ca

Present result

- No = Sr
- No yield is higher than Sr and Ca

No complex would be more stable ?

[11] L. G. Silén, A. E. Martell, (Eds.) Stability constants of metal-ion complexes. London: The Chemical Society (1964).
[12] R. D. Shannon, Acta Cryst. 32, 751 (1976). [13] J. E. House, et al., Thermochemica Acta, 66, 365-368 (1983).

15

Results and discussion ²⁵⁵No

Calculation for sulfate of group 2 elements and No

硫酸錯体と金属イオンの電荷計算結果^[9]

	Electron configuration	Charge of metal
MgSO ₄	[Ne]3s ^{0.04} 5p ^{0.01}	1.94
CaSO ₄	[Ar]3d ^{0.01} 5s ^{0.01}	1.98
SrSO ₄	[Kr]4d ^{0.01} 6p ^{0.01}	1.98
BaSO ₄	[Xe]5d ^{0.01}	1.98
RaSO ₄	[Rn]7s ^{0.01} 6d ^{0.01}	1.85
NoSO ₄	[Rn]7s ^{0.04}	



構造最適化された硫酸錯体

ソフト: Gaussian 16 rev. C
汎関数: B3LYP
基底関数: 6-31G* for Mg, Ca, S, O
SDD for Sr, Ba, Ra, No

Noの6d軌道が寄与した“Noの共有結合性”
(Covalent bonding for No)

Covalent bonding of No would contribute to stability of sulfate complex of No => Higher K_d value than expected

[9] 遠水翔 大阪大学大学院理学研究科修士論文 (2021).

7

Recent researches on No

Co-precipitation method

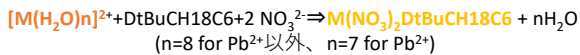
- Co-precipitation with samarium hydroxide
- Co-precipitation with barium sulfate
- Co-precipitation with calcium oxalate
- Co-precipitation as malonate

Solid-liquid extraction

- Extraction by crown ether resin
- アームドクラウンエーテル樹脂

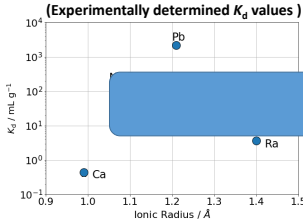
7

Results of extraction exp. of No

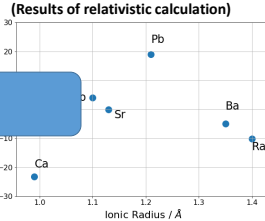


の反応における各分子のエネルギーを、相対論的量子化学計算によって求め、反応エネルギーを調べた

Sr レジン/3.5 M硝酸系の分配係数



相対論的量子化学計算による計算値



Consistent values with the experimentally determined ones were obtained by relativistic calculation
=> Success in modeling

7

Summary

- 重アクチノイド元素、ノーベリウムの化学研究を **実験** と **理論** の両面から進めている。
最近、硫酸バリウム共沈挙動やSrレジン抽出挙動の研究をノーベリウムに対して実施することができた。
(We have performed experimental and theoretical researches on nobelium. Here, I present the investigation of nobelium sulfate)
- 硫酸バリウム共沈実験では、Noが硫酸バリウム沈殿と共沈することが分かった。イオン半径を大きく反映する実験においてNoはCaとSrの中間の抽出率を持つといった結果が得られていたが、本研究では2族元素とは異なる“Noの共有結合性”を支持する結果を得られた
(It was found that No forms coprecipitate with barium sulfate and the yields were higher than those of Ca and Sr. Higher stability of the No complex may be due to covalent bonding between No and sulfate ion)

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謝辞

この場をお借りして、本研究を行うにあたり多大なるご支援を賜りました方々に厚く御礼申し上げます

^{133}Ba の製造

理化学研究所仁科加速器センター
加速器オペレーターの皆様
大阪大学核物理研究センター
加速器オペレーターの皆様

^{255}No の加速器オンライン共沈実験

大阪大学大学院理学研究科
大高 咲希 様、渡邊 瑛介 様、中西 諒平 様、速水 翔 様、益田 遼太郎 様、
王 瑞麟 様、板倉 悠大 様
理化学研究所仁科加速器センター
羽場 宏光 博士、重河 優大 博士、YIN Xiaojie 博士、南部 明弘 様、
加速器オペレーターの皆様

サレジオ工業高等専門学校
横北 卓也 博士

19

Question and answer session

Q: Is it possible to have pure divalent in a nobelium complex?

A: Norberyllium is rather divalent stable.

Q: Is it also divalent in complexes?

A: Basically, it is stable in divalent form, and it is difficult to oxidize it the other way around. Some of the electrons from the nitrate ion seem to flow into the d-orbital of nobelium, forming a covalent bond.

Q: How many atoms of nobelium are used in the experiment?

A: A few atoms or 10 atoms.

Q: Regarding electrochemical reactions, if divalent is the most stable form of Nobelium, how many volts are used for divalent/trivalent?

A: About 1.3 V. It has already been reported and I am a co-author.

Q: It is very interesting that no-beryllium works like a binary genus. Does Lawrencium work like three genera?

A: Yes. Actinium and lawrencium are very similar. Just one d, two s and one d. There are some systems in which I see a tremendous difference between lawrencium and actinium, and I am interested in what makes them different, not the other way around.

Q: This is just a commentary, but this is the way you approach even ionic radii, for example, with such a small sample. I was surprised. No, thank you very much indeed.

A: Really, thanks to the development of computation, we can finally have a discussion.

2.10 T. Yoshimura (IRS, Osaka Univ.)

Introduction to Institute for Radiation Sciences, Osaka University

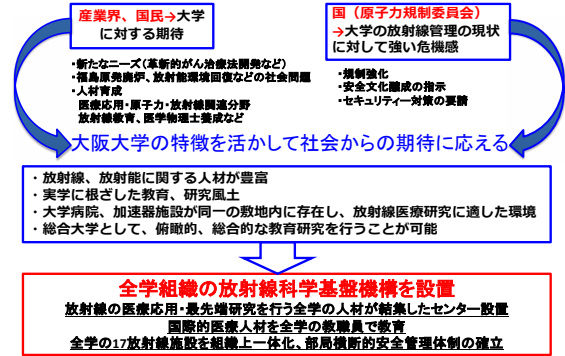
大阪大学放射線科学基盤機構の紹介

Introduction to Institute for Radiation Sciences, Osaka University

Radioisotope Research Center,
Institute for Radiation Sciences
Takashi Yoshimura



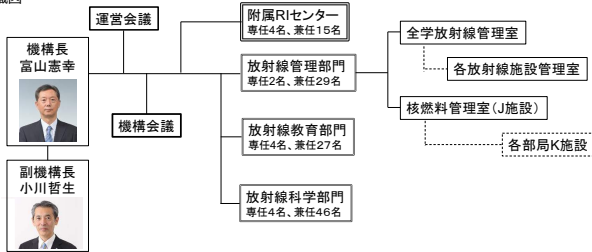
平成30年設立時における背景・課題(放射線安全管理、教育研究)



放射線科学基盤機構の取り組みと全体組織図

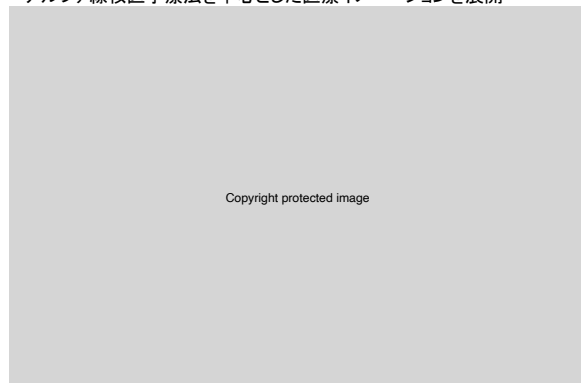
- ・全学横断的な放射線管理体制、全学連携の安全セキュリティ体制の構築
- ・放射線・原子力に関する教育資源の共有、全学的な教育プログラムや人材育成プログラムの提供
- ・部局横断的放射線関連教育研究プロジェクトの推進
- ・アルファ線核医学療法を中心とした医療イノベーションの展開
- ・放射線・原子力分野に於いて共同利用・共同研究、産学共創の推進、及び国際機関や関係省庁との調整や連携、全国の放射線施設の連携拠点化の推進
- ・施設統合・機能集約:理学研究科の2放射線施設とRIセンター(豊中)の放射線事業所統合、医学系研究科の放射線施設とRIセンター(吹田)の統合

組織図



放射線科学部門のミッションと活動

部局横断的放射線関連教育プロジェクトの推進
アルファ線核医学療法を中心とした医療イノベーションを展開



取組の総括

- ・本機構は、学内の放射線施設を一元化する我が国初の組織として平成30年4月に設置
- ・「アルファ線核医学療法開発プロジェクト」に注力し、当初設定した到達目標である「候補薬剤の決定」を大幅に上回り、4年目にあたる本年度に医師主導治療を阪大病院で開始する段階に到達

<研究>

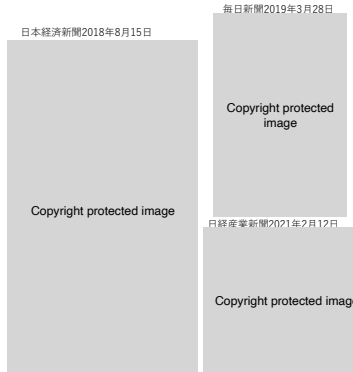
1. アルファ線核医学療法開発プロジェクト
2. 分野横断研究の推進

<教育>

- ・全学の放射線教育プログラムを順調に構築
1. 放射線教養と研究人材育成プログラム
 2. 国際教育・人材育成プログラム
 3. 放射線安全教育ならびに管理人材育成

<安全管理>

1. 全学安全管理体制の構築
2. 吹田地区、豊中地区でのRIセンターと医・理の放射線事業所統合



Question and answer session

Q: Is the program for undergraduates in Human Resource Development a College of Liberal Arts program?

A: That's right; it is primarily for first-year students and covers the basics. In fact, after going to Fukushima and receiving training, we hope that second-year students will be educated and become more knowledgeable.

Q: The lectures for graduate schools include the Graduate School of Science, but is the main focus on doctors?

A: The main focus is on the Faculty of Science. Plus, it includes education and lectures for health science majors in the School of Medicine.

Q: I thought it was an opportunity for medical students to get an education since it is even clinical with astatine.

A: The main focus is on the health sciences. At the moment, we have not yet reached the point where medical students are coming to take the course.

Q: In the area of safety management, I understood that there is a move to separate and manage RI and nuclear fuel cleanly and clearly. Is this a decision that will work better?

A: First of all, the legal systems are different, so it is easier to understand if they are separated. However, those who actually use nuclear fuel are also those who always use RI and have in-depth knowledge. Therefore, the actual situation is that although they are separated, they are well managed within the company.

2.11 Y. Sakurai (KURNS, Kyoto Univ.)

Report on Survey of Hot Labs and RI Studies in the U.S. (1)

Report on the Inspection and Investigation of the Hot Laboratory in the U.S.A. (1)

Yoshinori Sakurai



Division of Particle Radiation Medical Physics,
Particle Radiation Oncology Research Center,
Institute for Integrated Radiation and Nuclear Science, Kyoto University

1

Purpose

- Investigation of the design, operation, utilization, etc. for major research reactors in Europe and USA, and discussion with the concerned persons, in order to reflect in the future detailed design of the newly-installed research reactor.
- In addition, inspection of RI production facility, biological irradiation facility, hot lab, etc..

2

Member

Institute for Integrated Radiation and Nuclear Science, Kyoto University (KURNS)

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Kazufumi TSUJIMOTO (Nuclear Science and Engineering Center,
Nuclear Science Research Institute)

Sho TOKUNAGA (Department of Research Reactor and Tandem
Accelerator, Nuclear Science Research Institute)

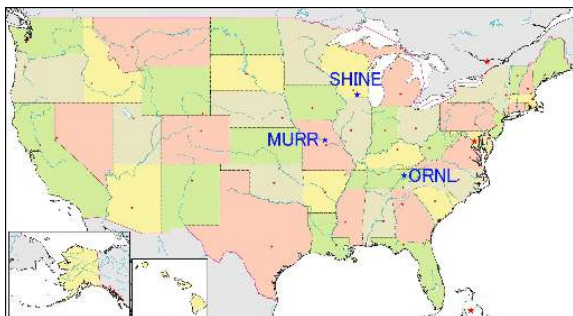
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Trip Period and Visit Destination

- Trip Period :
February 20, 2023 (Mon) - February 26, 2023 (Sun)
- Visit Destination :
 - MURR (University of Missouri Research Reactor):
Columbia, Missouri 2/21 (Tue)
 - ORNL (Oak Ridge National Laboratory):
Oak Ridge, Tennessee 2/23 (Thu)
 - SHINE Technologies: Janesville, Wisconsin 2/24 (Fri)

4

Location of Visit Destination



5

Flight Route (2/20)



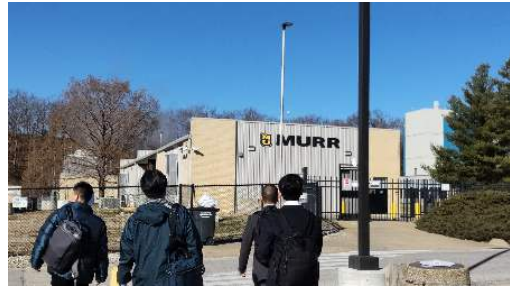
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MURR (1)

- University of Missouri Research Reactor
- Reactor power : 10 MW_{th}
 - *Largest university-owned research reactor in USA
- Fuel : Highly enriched uranium (93% enrichment)
- Reflector : Beryllium and graphite
- Operation : 1966- *20-year license renewal in 2017
- Production of various RI including medical use
 - *Consignment by companies, etc.
- Research facility for neutron capture therapy (NCT)
 - * The XVII International Congress on Neutron Capture Therapy (ICNCT-17) was held in October 2016

7

MURR (2)



Entrance of MURR

8

MURR (3)

Schedule

- 10:00 am Kyoto University team arrives
- 10:15 am Welcome & Introductions
- 11:00 am Overview of MURR presentation
- 11:30 am Lunch
- 1:00 pm MURR Facility Tour
- 2:30 pm Discussion and Q&A
- 4:00 pm Adjourn

Guided by Mr. Chris Dohm (Manager of Special Projects Group) and 7 other persons +α



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MURR (4)

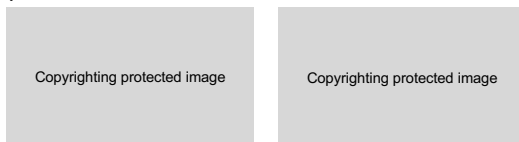


Outline of MURR (From HP and cover of notebook)

10

MURR (5)

- Hot laboratories
- Manufacturing RI separation processing in hot cells
- Quality system, infrastructure, staff and skills to provide full GMP (Good Manufacturing Practice) products and services

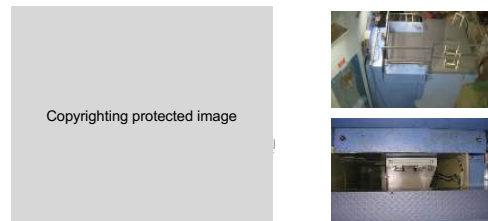


Outline of hot laboratories (From HP)

11

MURR (6)

- Research facility for NCT
- Si-Bi filters, thermal neutron flux : $8.4 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$
- Shutter and irradiation system that moves up and down



Outline of research facility for NCT

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MURR (7)

- Research :
Life Sciences, Material Sciences, Social Sciences, Research Isotopes & Radiochemicals
- Education :
Graduate & Undergraduate Programs in Engineering, Chemistry, Physics, Biochemistry, Arts and Science
- Operation : 6.5 days / 1 week, 52 weeks / 1 year
- Annual budget : 15% MU funding, 85% self-generated

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Flight Route (2/22)



14

ORNL (1)

- Oak Ridge National Laboratory
- High Flux Isotope Reactor (HFIR)
- Reactor power : 80 MW_{th}
- Fuel : Highly enriched uranium (93% enrichment)
- Reflector : Beryllium
- Operation : 1965-
- Production of various RI including medical use
- Production of Pu-238, etc..

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ORNL (2)



ORNL Visitors Center

16

ORNL (3)

Schedule

- 10:00AM Pickup/Meet Visitors
- 10:15AM Welcome and Introductions
- 10:30AM Presentation: New Radioisotope Production Research Reactor Project (Dr. Yamamura)
- 11:30AM HFIR Facility Tour
- 12:15PM Travel to Cafeteria
- 12:30PM LUNCH
- 1:30PM 4501 Facility Tour
- 2:15PM Travel to Melton Valley
- 2:30PM 7920 Facility Tour
- 3:15PM Discussions Closeout Meeting
- 4:00PM DEPART ORNL

Guided by Dr. Chris Bryan (Section Head of RI Production Engineering & Analysis) +α

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4:00 PM	DEPART ORNL

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ORNL (4)

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Outline of HFIR (From HP and leaflet)

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ORNL (5)

- Hot laboratories
For medical RI, separation processing of I-131, Mo-99, Ac-227, Lu-177, etc.



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One of hot laboratories

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ORNL (6)

- Research :
 - Biological Materials and Systems
 - Chemistry, Geochemistry and Environmental Science
 - Computing, Modeling, and Data Analytics
 - High Pressure Science
 - Materials and Engineering
 - Quantum Materials
 - Soft Matter and Polymers



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Flight Route (2/24)



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SHINE Technologies (1)

- Subcritical Hybrid Intense Neutron Emitter → SHINE
- Subcritical system device combining DT reaction and uranium solution
- Production of medical Mo-99
- Under construction of a large-scale production facility. Target to start operation in 2024
- Also, production facility of medical Lu-177
- Industrial use of nuclear fusion system
- Wisconsin actively attracts venture companies
→ Innovation Court, Innovation Drive

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SHINE Technologies (2)



Entrance of SHINE

23

SHINE Technologies (3)

Schedule

- 12:00am Meet & Greet SHINE HQ
Introductions
- 2:00pm Travel to and tour Chrysalis (Mo-99 Production Facility)
- 3:00pm Q&A, closing comments
- 4:00pm Guests depart

Friday, Feb 24		
Time (GMT-05:00)	Agenda Item	SHINE Participants
12:00 - 12:30 pm	Meet & Greet SHINE HQ Introductions	Greg Piefer, Greg Piefer, Todd Asmuth, Greg Piefer, Greg Piefer
2:00 - 3:00 pm	Travel to and tour Chrysalis (Mo-99 Production Facility)	Greg
3:00 - 3:30 pm	Q&A, closing comments	Greg, Todd, Greg
4:00 pm	Guests depart	

Guided by Dr. Greg Piefer (CEO & Founder) and Mr. Todd Asmuth (President & Chief Strategy Officer) +α

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SHINE Technologies (4)



Outline of one of the neutron generation systems (From HP)

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SHINE Technologies (5)

- Eight units installed in the production facility under construction
- Adjacent to a small airport
→ Products are transported by plane
- Competitors are also nearby



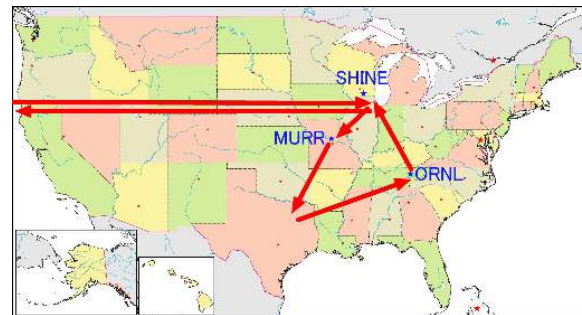
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Flight Route (2/25)



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Whole Flight Route



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Summary

- Visited three locations such as MURR, ORNL, and SHINE
- Felt the scale of activity related to RI production and the degree of availability of the related facilities, especially the hot laboratories, in USA.
- Impressive that 85% of MURR's annual budget was self-generated related to RI production.
- Expect that the knowledge obtained from this inspection visit will be reflected in the detailed design of the new research reactor.

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2.12 H. Yoshinaga (KURNS, Kyoto Univ.)

Report on Survey of Hot Labs and RI Studies in the U.S. (2)

米国ホットラボ視察・調査報告 (2) Report on the hot laboratory in the USA(2)

京都大学複合原子力科学研究所 技術室 吉永尚生
KURNS, Kyoto Univ. Hisao Yoshinaga

1

Payed Attention to 着目したところ

- Management of Hot Laboratory(HL)
- How they product RIs & Facilities for those Processes
- Work style of Staffs

2

MURR

次代へのSDGsな飛躍

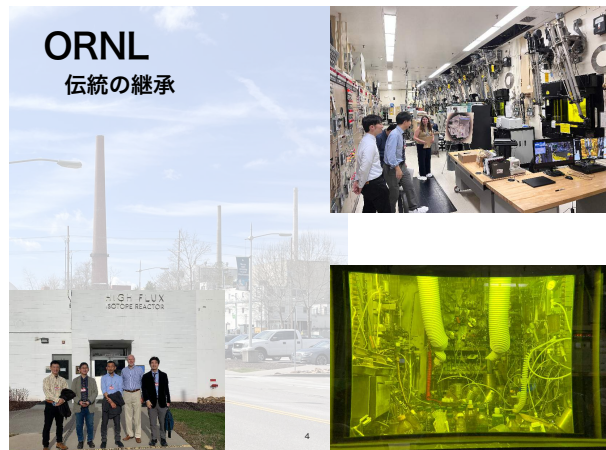
- No Photo
- Whole the Building is Radiation Control Section
- Even the Front desk
- Every staff were specialized for single work.
Operator, Manufacturer, economist, Researcher etc.
- Operator Trainie needs about 2 years
- Developing Facility with all the MU.
- Only short Movie for HL of RI production



3

ORNL

伝統の継承



4

SHINE Tech. Inc.

- Simple Facility for Irradiation



5

Summary

Fukui炉のまえに

- Plan of how activate KURNS is the most prior to post KUR especially on RIs Production.
- Effective utilization and economic circulation



2.13 T. Yamamura (KURNS, Kyoto Univ.)

Discussions on facilities

Dr. Sakurai's official summary and Mr. Yoshinaga's talk on the technical aspects and lifestyle were comprehensive and interesting. Both MURR and HFIR, which we inspected this time, are almost the same age as KUR and continue to be active. I felt that it is a pity that KUR is shutting down with these MURR and HFIR behind it. The hot labs are also really interesting, like a museum already. In one cell, they are separating molybdenum-99. Next to that is plutonium-238, next to that is separation and production of californium, and next to that is extracting einsteinium, which is being moved to the US and Japan for study. It is not the most up-to-date, but it is very organized and used. In Oak Ridge, for example, not only actinium-227, but when it comes to 225, for example, it is produced at BNL and moved. So it is not necessarily that they only handle what they manufacture at their own facilities. In this sense, the method of transportation was very important. We were actually shown a number of things. I was surprised to see that the drums that we normally use to store waste were used for transportation between BNL and ORNL. Another thing that stood out was the difference in the correspondents MURR is very business oriented, and the business unit people explained to us how they do business. Oak Ridge was really well-known and was handled by prominent researchers. SHINE, the last one, was addressed by the CEO of the company's founder. These people will be giving their presentations tomorrow, so I hope everyone will listen to them.

Any comments or suggestions?

Q: One thing that particularly surprised me was the very high rate of operation at the University of Missouri. Another thing is that it is 85% funded. It seems more like a commercial reactor than a university research reactor. Does high availability of university research reactors lead to high research performance?

A: I have only heard about the BNCT related to myself, but it seems that they have a facility and use it mainly for animal experiments for drug development. They also do about 200 animal irradiations a year, and the activity is high not only for RI production but for other research as

well.

Q: Does the fact that you are allocating people to RI production mean that you have a separate staff for that purpose?

A: Yes, I think so, because RI production is basically a process in which the samples are irradiated as soon as they are placed, so we are making good use of that characteristic.

Q: Can it be operated continuously for that long? How do you maintain it?

A: The RI system does not need as much maintenance as in Japan because it is not tied down by the regulatory agency. 5 operation teams work in shifts and do maintenance as they notice things, and if necessary, they stop the system from time to time to do maintenance. We don't have a period of time where we do inspections, and we don't operate from one month to the next. Also, the research reactor itself is very simple and they don't think it is necessary to take that much time.

Q: Is it possible to produce so much RI because you don't stop?

A: We are able to keep the time and continue continuous production in this way. This is what I saw as leading to a stable supply.

Q: It would be nice if this kind of thing could actually be done with new research reactors, but I wonder if it is difficult to do so in Japan.

A: I think so.

Q: At Oak Ridge, there were many hot cells in a row.

A: Probably not all of them are in operation. The cells that are being dismantled to recycle fuel, and the ones that will become the main pellets at the end, are probably brought in from other places and used in the final assembly process. The other parts of the plant are still in operation, but the picture shown in the previous section is not as good as it could be. Some of the cells looked as if they had been disassembled long ago and left there for a long time. The

MURRs are designed for easy removal and replacement of fuel underwater, while the HFIRs are one-piece units.

Q: Wasn't the MURR originally designed for RI production?

A2: I don't think so. There are holes of various sizes and various irradiation methods. Among them, there were pneumatic tubes similar to our pneumatic tubes, and there were also ones that were equivalent to long-term irradiation. In this situation, there was a period of decline as a research reactor and research facility, and in order to earn compensation, we devised a way to use the money earned from the manufacture and sale of RIs to cover the maintenance and research budget. The situation is similar to ours.

Q: It would have been good for KUR if we could have followed your example.

A2: I think each country has its own way of thinking, so it is not something that can be imitated in general, but I would like to do my best.

Q: Regarding the SHINE story, if RI can be produced in a critical reactor, is the trend that it does not have to be a nuclear reactor?

A3: I would like you to listen to the SHINE talk tomorrow. They are a company that does not rely on nuclear reactors, and specializes in continuing production by a single company.

Q: Regarding SHINE's use of the DT reaction to produce neutrons, since the DT reaction uses tritium, I am interested in a system that does not leak tritium, such as a glove box. If it is not such a system, then it needs to be adapted to Japanese regulations.

A: In fact, I could see the confidence that they are making something that is viable as a system, in the form of flying it in jet form and hitting the accelerated D. The founder of the company originally studied fusion research in graduate school and earned a degree.

Q: Now you're talking about a system that uses an accelerator to hit the material with deuterium, probably tritium. Why is it necessary to combine it with a subcritical reactor? If you can place

a system that does not use a subcritical reactor, the idea is that you can build a manufacturing base in a place where you cannot place a research reactor.

A: I was originally interested in the SHINE system because I studied ADS. As for tritium, we are making people inhale tritium gas, and then accelerating neutrons to separate the tritium. The neutrons that come out are used to spark a fission reaction in the subcritical system to start operation. But on the other hand, a company called NorthStar, also in Wisconsin, started lutetium production here at the University of Missouri using the capture method. In parallel with this, they are thinking of using an accelerator to produce the original lutetium. In the future, we are thinking of going uranium-free, as you mentioned, and aiming to produce molybdenum using only an accelerator and molybdenum without using uranium. I think the idea I mentioned earlier is possible. However, at the moment, we are working on the production of molybdenum by uranium fission because it is more reliable.

Q: Is it correct that the reason you are using a subcritical reactor is simply to produce molybdenum-99?

A: Yes, that is correct.

Q: So if you were not limited to molybdenum-99, you might be willing to move toward such a system?

A: If, for example, the main focus were to produce actinium together, that could be possible. Right now, we are doing it because it is convenient to recover molybdenum from fission.

Q: In your first presentation, Mr. Sakurai, you mentioned that only highly enriched fuel is used, but I assume that the Fukui site will not be highly enriched. What kind of fuel will be used will depend on what you want to achieve and the use of the hot laboratory. For example, there are reports of reprocessing of fuels other than uranium oxide, such as silicide fuel and molybdenum fuel, and in France and other countries, there are reports of reprocessing of small amounts of different fuels in research reactors, and such research is necessary. If possible, it would be nice if the Fukui Reactor is capable of such research. If you have anything to share

about this, please let us know.

A: First of all, the fuel used in the new research reactor in Fukui is 20% enriched Max fuel. We cannot use highly enriched uranium like in the United States. There is some debate about whether nuclear fuel can be used in a hot lab. If there is a strong request, I would be willing to consider it.

Q: Thank you. If there is such an opportunity, I would like to experiment.

A: I would like you to raise the request.

Q: If you were to conduct an experiment using uranium, how much would you need?

A: I don't usually use grams. If we could do about a gram, that would be great.

Q: We have also requested to use nuclear fuel in the hot laboratory in Fukui, and although it may be less than a gram order, we have requested to be able to conduct small-scale experiments.

Q: After your visit to the U.S., how do you handle waste? I have heard that a large facility would produce a tremendous amount of waste. When I did experiments at the Idaho National Laboratory, they were not concerned about waste at all, so that is considered the biggest difference between Japan and the U.S. This is an opportunity to show that when we create something new, we also need to work together to establish laws for the disposal of the waste from the experiments. Material informatics is useful because it is necessary to reduce waste. What was the US like in this area?

A: Oak Ridge has plenty available, and the situation is completely different from Japan, so if you want to conduct such experiments, you will have to go to the US. When a system for waste disposal at research institutes and other facilities is established, there is a possibility that waste could be disposed of more smoothly, but the high cost will never change. That is a little different from a place where there are many facilities in the desert and we don't have to worry so much about waste.

Q: Thank you very much. We need more young Japanese actinide researchers to conduct experiments at overseas facilities and bring their findings to us, and we need to increase the number of collaborators. I may have a different point of view, but experiments in the U.S. should be conducted separately from the situation in Japan.

A: It would be good if we can establish a win-win relationship with the INL and other institutions in the U.S.

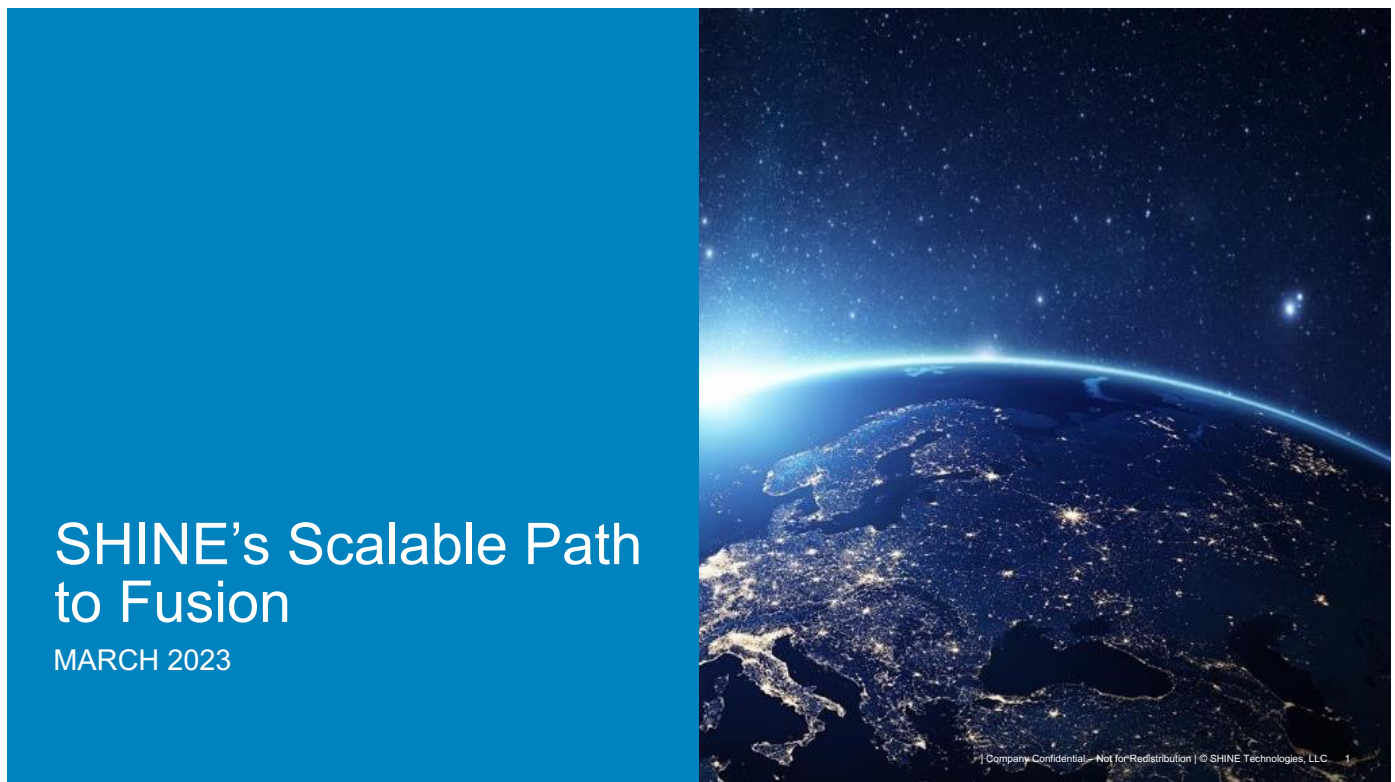
2.14 M. Nakase (Tokyo Inst. Tech.)

Opening of 2nd-day Discussions

Good morning, everybody. I am Masahiko Nakase from Tokyo Institute of Technology. Thank you very much for joining this interesting meeting. Today we have some English speakers from US.

2.15 Greg Piefer (SHINE Technologies, Inc.)

Plan and prospect of SHINE Technology



Question and answer session

Q: Do you have any special techniques or new ideas to ensure adequate separation of critical products?

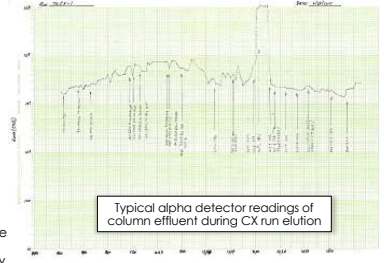
A: We actually made a test batch of Mo-99 and GE was able to test it in a dry generator and prove that it is equivalent to Mo-99 made in a nuclear reactor. Basically, what we are using is what has already been published.

Q: Scientists have shown the effectiveness of Ac-225 for cancer treatment in 2016; do you have plans to produce alpha-radiators?

A: However, we prefer to focus on what we're uniquely good at. We knew we could concentrate ytterbium in-house, and that combined with our ability to produce neutrons and perform advanced separation gave us good technology to scale up production, and we had an inherent advantage over other producers.

Transcurium element separations via cation exchange elution using AHIB

- Conversion from chloride form to nitrate by hydroxide precipitation, filtration, and re-dissolution in HNO₃
- Elemental separation by ammonium alpha-hydroxyisobutyrate (AHIB) at varying values of pH
- Column is heated ~70°C
- Element (band) separation followed with neutron and alpha probes
- Key is small, uniform particle size of resin and high pressure operation to achieve good flow rate



Some major scientific impacts of the heavy element products

Discovery of new heavier elements and isotopes using heavy element radionuclides as accelerator/cyclotron targets

Basic research on the physics of heavy elements

- Electron behavior in orbitals
- Nuclear properties
- Nuclear reactions

Discovery of bimodal fission in some nuclides with Z ≥ 100

Basic research on the chemistry of heavy actinides

- Chemically stable compounds
- Crystal structure of salts
- Solution chemistry
- Spectroscopy

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²⁵²Es (0.17 mg, self-illuminated)

The heavy element program was endorsed twice by the National Research Council

100+ publications resulted each year from research using heavy element products

E.K. Hulet, "Bimodal Symmetric Fission Observed in the Heaviest Elements," Phys. Rev. Lett. 56, 313-316 (1986)

OAK RIDGE National Laboratory 8/20 February 2023 Seminar

Promethium: ORNL's First Elemental Discovery

- Isolated in 1945 (ORNL) from irradiated uranium by Joseph A. Marinsky, Lawrence E. Glendenin, and Charles D. Coryell
 - Announced in 1947 at the ACS meeting in New York City
- Name suggested by Charles Coryell from the Titan Prometheus
 - Prometheus stole fire from Mt Olympus and brought it to humans in Greek mythology
 - Reminiscent of how promethium is made in nuclear reactors

Joseph Marinsky Lawrence Glendenin Charles Coryell

¹⁴⁷Pm, Van Lys Promethium Isotope, Power Graph Sheet, 1945, Pacific Northwest Laboratory, Richland, WA, BNWL-45

OAK RIDGE National Laboratory 8/20 February 2023 Seminar

Promethium-147 is a High Demand Radioisotope

- ¹⁴⁷Pm is used as a beta gauge, in radio-luminescent paints, and nuclear batteries
 - 2.62-year half-life
 - 927 Ci/g
 - Decays via β⁻ emission (62 keV avg) to ¹⁴⁷Sm
 - γ-emission @ 121.220 keV 0.00285 % intensity
 - Considered a pure β⁻ emitter
- Formerly produced at the Mayak Production Association
- US has not produced ¹⁴⁷Pm in over 50 years
 - Last production was at the fission product plants at INL, ORNL, and PNNL by isolating from irradiated uranium
- ORNL dispensed ¹⁴⁷Pm from these fission plants

OAK RIDGE National Laboratory 8/20 February 2023 Seminar

Historical Production of ¹⁴⁷Pm

- Fission product plants in US separated lanthanides from irradiated U fuels
- Ion exchange, oxalate precipitation and recrystallization
 - Multi-stage recrystallizations
 - Solvent extraction
 - Ion Exchange
 - Zinc-displacement IX
- G. W. Parker and P. M. Lantz purified 4.5 mg in 1948
- F. Weigel and co-workers later produced Kg quantities
 - First to make elemental metal

OAK RIDGE National Laboratory 8/20 February 2023 Seminar

Separations Development in 1969

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812. Z 1124-COLUMN SYSTEM DEC 28 1969

Low, DP-1194, 1969

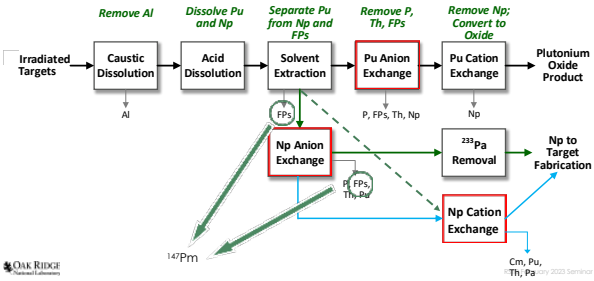
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818. Z 1487-SEPARATION OF FEEL-113LPS 5/17/71

OAK RIDGE National Laboratory 8/20 February 2023 Seminar

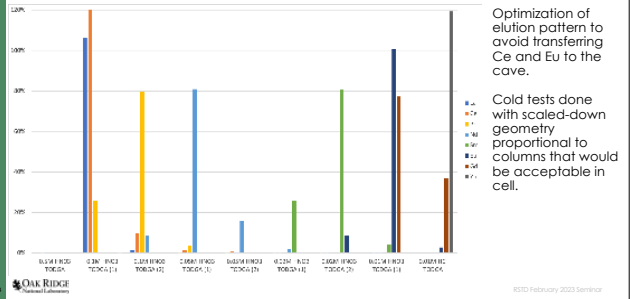
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Overall flowsheet Pu-238 production – Pm harvesting



Promethium Project – “Cold” Test

Hot Cell recovery of Pm from Pu campaign wastes.



Optimization of elution pattern to avoid transferring Ce and Eu to the cave.
Cold tests done with scaled-down geometry proportional to columns that would be acceptable in cell.

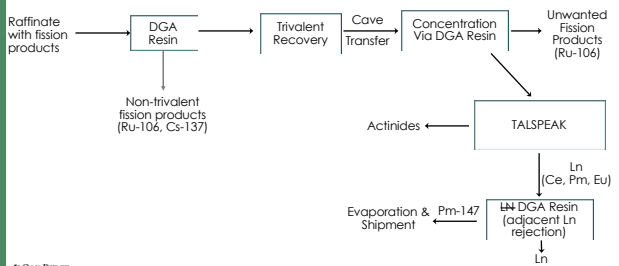
Continuous Improvement



Three Hot Cell runs so far

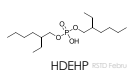
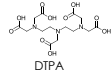
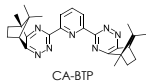
Run 1 (P4 Demonstration)	Run 2 (P4-2 Recovery)	Run 3 (P5)
6 L of raffinate	60L of Raffinate	130L of Raffinate
290 mL Resin	290 mL Resin	250 mL Resin
Elution by HNO ₃ & HCl	Elution by HNO ₃ & HCl	Gradient HNO ₃ Elution
Eluted ¹⁴⁷ Pm in HCl	Eluted ¹⁴⁷ Pm in HNO ₃ with 98.9% rejection of ¹⁴⁴ Ce & 96% rejection of ¹⁵⁵ Eu	Eluted ¹⁴⁷ Pm in HNO ₃ with 99.7% rejection of ¹⁴⁴ Ce & >99.5% rejection of ¹⁵⁵ Eu

Pm-147 Processing Flowsheet



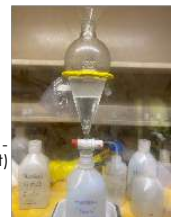
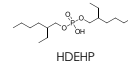
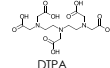
¹⁴⁷Pm Production: Solvent Extraction

- Removal of ²⁴⁴Cm from ¹⁴⁷Pm
- Use of camphor-bis(triazenylpyridine), CA-BTP
 - Works well
 - Experimental sample (no secure procurement)
- Cyanex 301
 - Bis-(2,4,4-trimethylpentyl)-dithiophosphinic acid
 - Degrades in nitric acid -> use dilute HCl
 - Excellent An rejection projected
- TALSPEAK



Trivalent Actinide Lanthanide Separation with Phosphorus-Reagent Extraction from Aqueous Complexes (TALSPEAK)

- Developed at ORNL in 1960's
- Separates actinides from lanthanides
 - Di-2-(ethylhexyl)phosphoric acid (HDEHP) in diluent (dodecane)
 - Lactate buffer with diethylenetriamine-N,N,N',N',N''-pentaacetic acid (DTPA, actinide holdback reagent)
 - Strip Ln from HDEHP/dodecane with strong acid



Continuous Improvement: Curium Removal

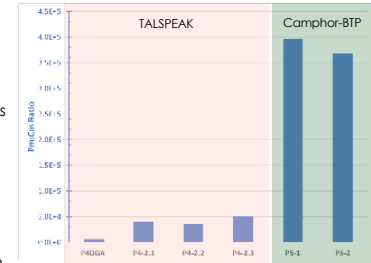
- TALSPEAK works, but...
 - Waste issues compound separation challenges
 - Severe ^{147}Pm losses during separation adding time and cost
- What options do we have?
 - Initial testing with an R&D sample of camphor-BTP showed promise
 - R&D sample from TN Tech
 - Residual from student research with L. Delmau, Kayron Rogers and Dale Ensor
 - Marshallton Labs contracted to produce camphor-BTP for larger testing
 - Development of Cm/Pm separation using BTP-based ligands begin at REDC

OAK RIDGE
National Laboratory

2023 February 2023 Seminar

TALSPEAK vs. Camphor-BTP

- TALSPEAK:
 - High product losses
 - Back extraction of ^{147}Pm
 - Law of diminishing returns
- Camphor-BTP
 - ^{244}Cm extracted
 - ^{147}Pm stays in aq phase
 - Decreased ^{147}Pm losses
 - Less time for separation
- Remember that gremlin...



OAK RIDGE
National Laboratory

2023 February 2023 Seminar

Promethium Project

Further purification of Pm from strong gamma emitters in Cave or Glove Box.

Separation of Pm from Am/Cm. Solvent extraction.

Polishing to reject adjacent lanthanides

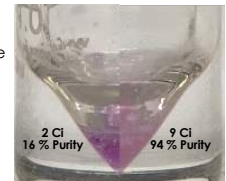
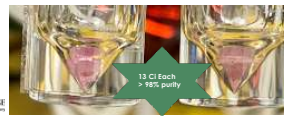


OAK RIDGE
National Laboratory

2023 February 2023 Seminar

Mining ^{147}Pm from Fission Products

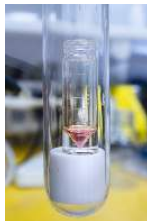
- Re-established the domestic ^{147}Pm production at ORNL
 - Revalorize ^{238}Pu waste stream
- ORNL is currently the only known supplier of ^{147}Pm
- Optimization on-going
 - An/Ln separation with BTP ligands
 - Adjacent Ln separation
 - Integration into the ^{238}Pu production schedule



OAK RIDGE
National Laboratory

Acknowledgments

- Emory Collins
- Dennis Benker
- Tony Dyer
- Thomas Dyke
- Matt Silveira
- April Miller
- REDC shift personnel
- REDC Shift Supervision
- Analytical Group



This work is supported by the US Department of Energy Isotope Program, managed by the Office of Science for Isotope R&D and Production.

OAK RIDGE
National Laboratory

Question and answer session

Q: For Pm-147 separations, how is the chemical purity checked after production?

A: ICP-MS can be used, but this only yields a maximum of 147, which may contain samarium-147 since it is a decay product. However, data can be measured and compared by liquid ventilation.

Q: When you ask me to obtain a heavy element, please let me know.

A: Which element or isotope are you interested in?

Q: I'm interested in ... That's about it.

A: Does that mean I need to make a request very soon? We will start the next California campaign. We will start the next campaign in three weeks; you will need to contact NDEC.

Q: How do we get Neptunium-237?

A: Neptunium-237 was produced in large quantities at Savannah River in the 1960s and then moved from Savannah River National Laboratory to Idaho National Laboratory, where it is stored. Basically, neptunium was produced at Savannah River as long ago as 1915.

Q: So it was stored by uranium radiation?

A: We don't know exactly how it was produced. I think it was probably produced by uranium irradiation, but I don't know the details of how it was produced 15 years ago.

2.17 Rob Hall (MURR, Missouri University)

Recent activities, systems, and facilities of MURR for radiopharmaceutical R&D

MU Research Reactor
University of Missouri

MURR[®]
Matters...

京都大学
KYOTO UNIVERSITY

Condensed-matter Chemistry in Actinides and their Applications / Production of medical RIs by Reactor Irradiation



March 3, 2023

Saving Lives, Creating Livelihoods... through Research & Education

MU Research Reactor
University of Missouri

MURR[®]
Matters...

Welcome to MURR[®]



Saving Lives, Creating Livelihoods... through Research & Education

MU Research Reactor
University of Missouri

MURR[®]
Matters...

Improving Quality of Life



"Cancer, unlike politics and religion is not a topic of controversy. No one is for it."
-S. Mloteky, 1989, A Snowflake in My Hand

Saving Lives, Creating Livelihoods... through Research & Education

MU Research Reactor
University of Missouri

MURR[®]
Matters...

University of Missouri Crown Jewel
MURR[®] is a Unique National Resource

- October 1966 = First Reactor Start-up
- Facility operates **24 hours a day**; **6 1/2 days per week**; **52 weeks a year** – *like no other!*
- 250 Full & Part-time Scientists & Staff
- 50 Students – Learning while helping!
- 20 Year NRC License granted in Jan 2017
- Modular Design
+ Replaceable Components
= **A Renewable Resource**



Saving Lives, Creating Livelihoods... through Research & Education

MU Research Reactor
University of Missouri

MURR[®]
Matters...

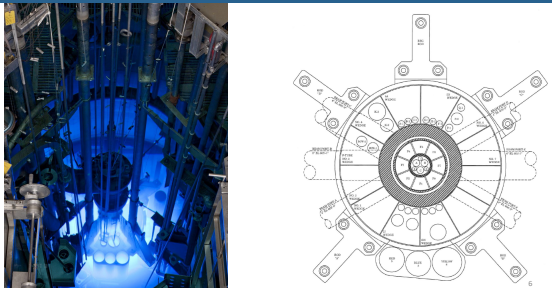
Leading Research Reactor
The most powerful of the Nation's 24 University Research Reactors

Facility	Power	Facility	Power
University of Missouri, Columbia (MURR [®])	10 MW	Kansas State University	250 kW
Massachusetts Institute of Technology	6 MW	Reed College	250 kW
University of California-Davis	2 MW	University of California-Irvine	250 kW
Rhode Island Nuclear Science Center	2 MW	University of Maryland	250 kW
Oregon State University	1 MW	Missouri University of Science and Technology (Rolla, MO)	200 kW
University of Texas, Austin	1 MW	University of Arizona	100 kW
North Carolina State University	1 MW	University of Florida	100 kW
Pennsylvania State University	1 MW	University of Utah	100 kW
Texas A&M University	1 MW	Purdue University	1 kW
University of Massachusetts-Lowell	1 MW	Idaho State University	5 W
University of Wisconsin	1 MW	University Of New Mexico	5 W
Washington State University	1 MW	Rensselaer Polytechnic Institute	1 W
Ohio State University	500 kW		

Saving Lives, Creating Livelihoods... through Research & Education

MU Research Reactor
University of Missouri

MURR[®]
Matters...



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MU Research Reactor University of Missouri MURR Matters...

Research & Development

Life Sciences

- ✓ Radiopharmaceutical Research
- ✓ Trace Element Epidemiology
- ✓ Plants Radiotracer Imaging
- ✓ Radioisotope Tracers

Material Sciences

- ✓ Triple Axis Spectrometer
- ✓ Neutron Reflectometer
- ✓ Multi-detector Powder Diffractometer
- ✓ High Resolution Powder Diffractometer

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Research & Development

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MU Research Reactor University of Missouri MURR Matters...

Education

Archaeometry

9

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MU Research Reactor University of Missouri MURR Matters...

Reactor Operations

- 6 person management staff
- 5 Operations Crews
 - 3-5 persons
 - 1 Lead Senior
 - 1 Senior
 - 1 Operator
 - 1 Trainee
- 12 hour rotating shifts
- Every 5th week is a training week

10

Saving Lives, Creating Livelihoods... through Research & Education

MU Research Reactor University of Missouri MURR Matters...

Products and Services

Each and every week MURR supplies the active ingredients for:

- TheraSpheres® - liver cancer
- Lutathera® - neuroendocrine tumors
- I-131 – thyroid cancer
- RadioGenix® - cardiac and bone scans
- Pluvicto® - prostate cancer

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Saving Lives, Creating Livelihoods... through Research & Education

MU Research Reactor University of Missouri MURR Matters...

Working Together

Academia and Industry Collaborating to Improve Lives

MURR Typical Fiscal Year

Funding Source	Percentage
MU Funding	85%
Self-Generated	15%

Blending all four MU mission elements:

1. Research
2. Education
3. Service
4. Economic Development

Academia and Industry Working Together

12

Saving Lives, Creating Livelihoods... through Research & Education

MU Research Reactor
University of Missouri

MURR Matters...

Targeted Radiotherapy & Diagnostics

NIDC NATIONAL ISOTOPE DEVELOPMENT CENTER
MANAGED BY THE U.S. DEPARTMENT OF ENERGY ISOTOPE PROGRAM

NOVARTIS

PLUVICTO™

ABKeye BIOMEDICAL

BWXT
(technetium 99m generator)

SHINE

Lantheus Medical Imaging

QUADRAMET
QUANITUM FOR PET/CT/SCANSIM ALGORITHM

NOVARTIS

LUTATHERA™

NorthStar
MEDICAL RADIOISOTOPES, LLC
(technetium 99m generator)

RadioGenix SYSTEM
(technetium 99m generator)

CardinalHealth
Iodine I-131 sodium iodide

Boston Scientific

TheraSphere™

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MU Research Reactor
University of Missouri

MURR Matters...

Main Hot Cell Facility

16.5 MeV Pet Trace Cyclotron

Irradiations Laboratory

14

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MURR Matters...

Mo-99 Hot Cells
(Intermediate Final Product)

CA Lu-177 Production Suite
(Active Pharmaceutical Ingredient)

35

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MU Research Reactor
University of Missouri

MURR Matters...

I-131 Production Suite
(Active Pharmaceutical Ingredient)

NCA Lu-177 Production Suite
(Active Pharmaceutical Ingredient)

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MU Research Reactor
University of Missouri

MURR Matters...

MURR's Future

37

Saving Lives, Creating Livelihoods... through Research & Education

MU Research Reactor
University of Missouri

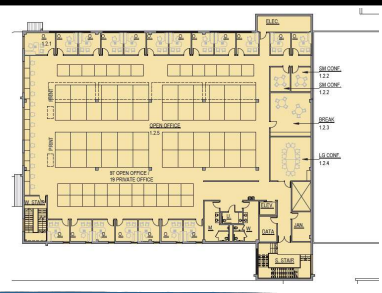
MURR Matters...

IRR Matters...

15,600 SF

38

Saving Lives, Creating Livelihoods... through Research & Education



MURR Nextgen

- One respondent said that the biggest risk to their supply chain is security of supply of medical isotopes like I-131, as medical isotopes cannot be stockpiled. When supply issues occur cancer patients don't get the required therapy to stop disease or lengthen and improve quality of life. To enhance security of supply of just in time medical isotopes an "in country - For country" approach is a good supply strategy.
- All respondents were of the strong opinion that the University of Missouri is the only partner capable of delivering on a new reactor in the US. All respondents echoed that the MURR reactor is world renowned for its uniqueness as the only reactor that runs 52 weeks a year where others are only operating maybe half of the time.
- Executives have confidence in MURR's reliability, scientific and safety expertise, their operational strength coupled with their ability to meet the commercial needs of industry, as they have done for decades, remains unmatched.
- "Building the new reactor at MURR is critical. The University has decades of experience running a reactor and of working with business. MURR has demonstrated that they can run a reactor in a way that meets the commercial needs of industry and have done so for decades."

Questions?



Question and answer session

Q: Do you produce elements other than iodine, molybdenum, and ruthenium?

A: Yes, we produce a variety of isotopes. Of course, these are the major drug-type isotopes we produce in large quantities. It depends on what the researcher wants to produce, whether it can be made in a reactor, and the reason for wanting to study it. It certainly does. We would encourage any university personnel interested in partnering with the University of Missouri Research Reactor to contact us and see where our interests align and where we might be able to collaborate.

Q: Do you produce other raw materials in your cyclotrons?

A: Our cyclotron is primarily used for pet imaging. We have access to it during off hours so that we can produce other isotopes. However, my specialty is not in the world of cyclotron production. So if you would like to send me an email, I would be happy to answer it.

Q: What do you think if you didn't have a reactor on campus, but could use other reactors like the HFTR and transfer isotopes produced from the HFTR? Would that work?

A: Actually, it is possible; the HFTR's powerful reactors irradiate the isotopes, which are then processed and distributed to researchers. So it is possible. In the future, we may be able to do much more. But what we want is to have our own 21 reactors running every week to better serve the medical ISO community. 15 min.

2.18 Toro Gonzalez (Oak Ridge National Laboratory)

Lanthanide-based and Poly(lactic-co-glycolic acid) Nanoparticles in Targeted Alpha Therapy

OAK RIDGE
National Laboratory

Lanthanide-based and Poly(lactic-co-glycolic acid) Nanoparticles in Targeted Alpha Therapy

Miguel Toro-Gonzalez, Sandra Davern
Oak Ridge National Laboratory
March 3rd, 2023

Users meeting on Condensed-matter Chemistry in Actinides and their Applications / Production of medical RIs by Reactor Irradiation

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

Motivation

Targeted alpha therapy vs. External beam therapy

- Specific targeting of tumor cells
- Enhanced therapeutic efficacy
- Reduce side effects
- Efficient treatment of cancer

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Motivation

Nanoparticles as radionuclide delivery platforms in targeted alpha therapy

Radioimmunoconjugates

Challenges

- Relocation of decay daughter(s) from tumor site
- Potential radiotoxicity to healthy tissues
- Decrease therapeutic efficacy
- Require higher activity/dose to achieve a therapeutic effect

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Outline

- Production methods for ^{225}Ac and $^{227}\text{Th}/^{223}\text{Ra}$
- Lanthanide-based nanoparticles
- Poly(lactic-co-glycolic acid) nanoparticles
- Targeted alpha therapy with nanoparticles
- Summary
- Acknowledgements

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National Laboratory

Production methods for ^{225}Ac and $^{227}\text{Th}/^{223}\text{Ra}$

ORNL perspective and experience

Production methods for ^{225}Ac and $^{227}\text{Th}/^{223}\text{Ra}$

Current production methods for ^{225}Ac

- Decay of $^{233}\text{U} \rightarrow ^{229}\text{Th} \rightarrow ^{225}\text{Ra} \rightarrow ^{225}\text{Ac}$
 - ORNL world's largest current producer (800-1000 mCi annually)
- High energy proton (80-200 MeV) spallation of natural Th targets
 - $^{232}\text{Th}(p, x)^{225}\text{Ac}$ reaction
 - DOE Isotope Program Tri-Lab Initiative BNL, LANL, and ORNL

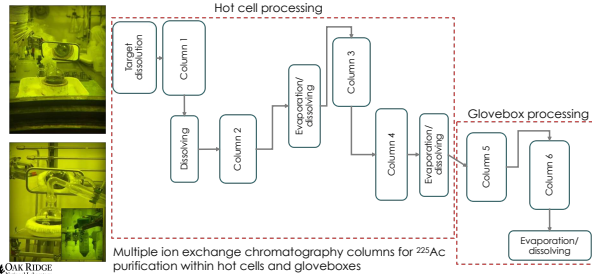
Methods in development involving reactor irradiation

- Production of ^{229}Th or ^{225}Ra via fast neutron irradiation of ^{230}Th or ^{226}Ra
 - $^{230}\text{Th}(n, 2n)^{229}\text{Th}$ and $^{226}\text{Ra}(n, 2n)^{225}\text{Ra}$ reactions
- Production of ^{229}Th by multiple and single neutron capture of ^{226}Ra and ^{228}Ra targets in a high flux nuclear reactor
 - $^{226}\text{Ra}(3n, 2\beta)^{229}\text{Th}$ and $^{228}\text{Ra}(n, \beta)^{229}\text{Th}$ reactions

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National Laboratory

Production methods for ²²⁵Ac and ²²⁷Th/²²³Ra

- Processing of ²²⁵Ac produced by high energy proton



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National Laboratory

Production methods for ²²⁵Ac and ²²⁷Th/²²³Ra

- ORNL is a qualified supplier of ²²⁷Ac to Bayer for Xofigo[®] production
- ²²⁶Ra targets are prepared from legacy medical devices
- Targets are irradiated in the High Flux Isotope Reactor
- Dissolution and processing of irradiated targets in hot cells and gloveboxes
- ²²⁷Ac is chemically separated and purified for shipment



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Lanthanide-based nanoparticles

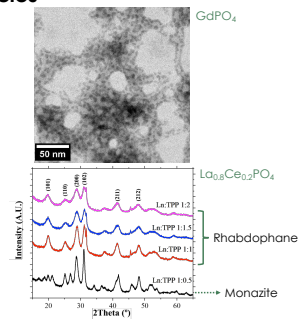
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Woodward et al. Bioconjugate Chemistry (2011)

Lanthanide-based nanoparticles

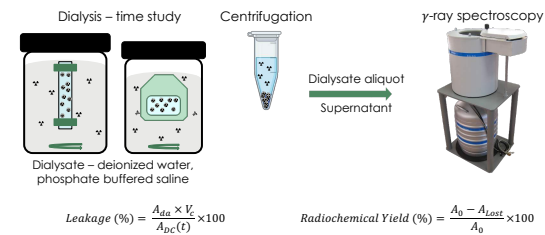
- Crystal structures with high resistance to radiation damage¹
 - Rhabdophane
 - Monazite
 - Zircon
- Potential to incorporate multivalent cations²
- Luminescence and magnetic properties



OAK RIDGE National Laboratory
1. J. Alloys Compd. 653, 279-289 (2015)
2. Radiochim. Acta 105, 761-784 (2017)

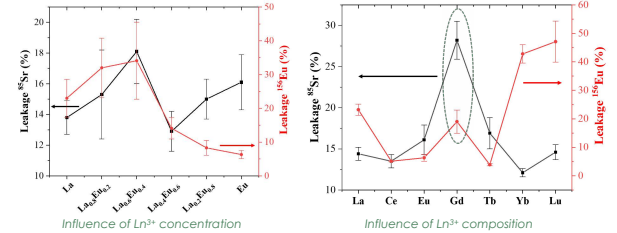
Lanthanide-based nanoparticles

Assessment of radioisotope encapsulation and retention



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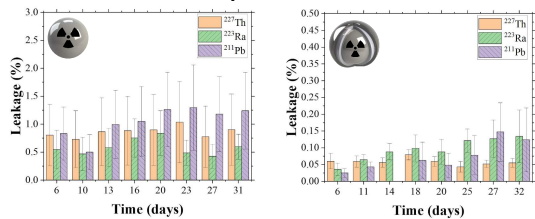
Lanthanide-based nanoparticles



- La_{0.9}Eu_{0.1}PO₄** - radioisotope leakage was influenced by radioisotope oxidation state (¹⁵²Eu³⁺ vs. ⁸⁹Sr²⁺)⁵
- LnPO₄** - ¹⁵²Eu³⁺ leakage influenced by Ln³⁺ ionic radii (higher of smaller Ln³⁺ = Yb³⁺ and Lu³⁺)⁵

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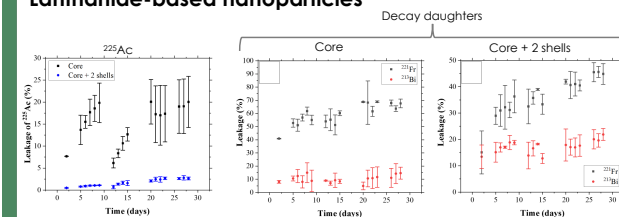
Lanthanide-based nanoparticles



- 10-fold decrease in radionuclide leakage after deposition of 2 shells
- $96.8 \pm 2.3\%$ and $94.4 \pm 3.8\%$ ^{227}Th radiochemical yield for core and core +2 shells

OAK RIDGE National Laboratory | Toro-González, M. et al. Nanoscale 12, 9744-9755 (2020)

Lanthanide-based nanoparticles

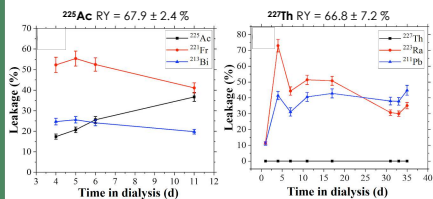


- Partial retention of ^{225}Ac , ^{223}Ra , and ^{213}Bi in $\text{Gd}_9\text{Eu}_2(^{225}\text{Ac})\text{VO}_4/\text{Gd}_9\text{Eu}_2\text{VO}_4$ nanoparticles
- ^{225}Ac retention was influenced by the formation of ^{225}Ac -citrate complexes
- ^{223}Ra retention is dependent on the number of shells
- ^{213}Bi retention is assumed to be affected by concentration of surface carboxyl groups

OAK RIDGE National Laboratory | M. Toro-González et al. Journal of Materials Chemistry B, 2018.

Lanthanide-based nanoparticles

Precipitation method – $\text{Gd}(^{225}\text{Ac})\text{VO}_4$ and $\text{Gd}(^{227}\text{Th})\text{VO}_4$

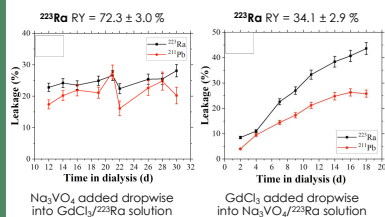


- Lower ^{225}Ac radiochemical yield in the precipitation method compared to citrate method
- Tetravalent actinide ^{227}Th is preferentially incorporated within xenotime structure
- Similar ^{227}Th radiochemical yield in both citrate and precipitation methods

OAK RIDGE National Laboratory | Toro-González, M. et al. Radiochim. Acta (2020)

Lanthanide vanadate nanoparticles

Precipitation method – $\text{Gd}(^{223}\text{Ra})\text{VO}_4$

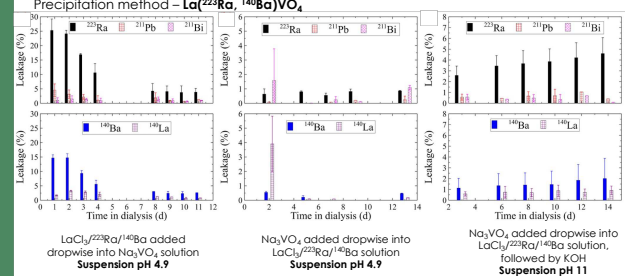


- Synthesis conditions influenced the radiochemical yield and retention of radioisotopes
- Precipitation of ^{223}Ra hydroxides leads to slow interaction with VO_4^{3-} species and continuous increase in leakage
- Precipitation method can be optimized to enhance radiochemical yield and decrease radioisotope leakage

OAK RIDGE National Laboratory | Toro-González, M. et al. Radiochim. Acta (2020)

Lanthanide-based nanoparticles

Precipitation method – $\text{La}(^{223}\text{Ra}, ^{140}\text{Ba})\text{VO}_4$



OAK RIDGE National Laboratory | Toro-González, M. et al. Journal of Nanotheranostics (2021)

Summary

- Encapsulation and retention of ^{223}Ra , ^{225}Ac , ^{227}Th , and decay daughters in lanthanide-based nanoparticles is influenced by:
 - Number of shells
 - Synthetic approach
 - Composition
- Targeted alpha therapy with nanoparticles shows promising therapeutic efficacy

OAK RIDGE National Laboratory

Acknowledgments

- Organizers of the Users meeting on Condensed-matter Chemistry in Actinides and their Applications / Production of medical RIs by Reactor Irradiation
- Research sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the US Department of Energy.
- A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.
- The GEM Fellow Internship Program at ORNL.
- DOE Isotope Program and REDC Laboratory Chemical Operations for supplying ^{225}Ac , ^{227}Th , and ^{223}Ra .
- ARM initiative team.

Question and answer session

Q: How the nanoparticle can interact with cancer cells?

A: I was showing here is when we work with nanoparticles, what interferes passive targeting or active targeting. In the passive targeting, blood circulation enables us to accumulate on the tumor. The regulator conjugates of targeting vector attached enables the nanoparticle to interact with cancer cells.

Q: I have a quite small question. In your second or third slide you showed us the Ac-225 emits five alpha particles. But as far as I know, Ac-225 emits four alpha particles.

A: Yes. So this last one that I include here, is Bismuth 209.

Q: I understand the benefits of nanoparticles, but at the same time I am curious as to how these nanoparticles are metabolized in the body. Is it easy to eliminate them?

A: Polylactic acid and glycol are metabolized by the body and broken down into lactic acid and glycolic acid. The question is, what happens to the nanoparticles? However, the challenge is that if they do not reach specific tumor cancer cells, the radionuclides are lost and may be targeted elsewhere altogether.

This will be wouldn't require a lot of study saying what's going to happen with those nanoparticles in your body.

2.19 Julie G. Ezold (Oak Ridge National Laboratory)

Radiochemical Processing at Oak Ridge National Laboratory


OAK RIDGE
National Laboratory

Radiochemical Processing at Oak Ridge National Laboratory

Julie Ezold
Cf-252 Program Manager
Oak Ridge National Laboratory

March 2023
Oak Ridge, Tennessee


ORNL is managed by UT-Battelle, LLC, for the U.S. Department of Energy.



OAK RIDGE
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Outline

- A Little Elemental History
- Discovery and Production
- What's Next



1869: Mendeleev's organization of the known elements

- Demonstrated trends/similarities by arranging elements in a two-dimensional network according to their chemical properties
- Reordered elements despite their accepted masses (early indication that atomic mass was not the determining factor)
- Allowed gaps in the table, predicting 10 new elements (7 actually exist)

In 1906, Mendeleev came within one vote of winning the Nobel Prize

Mendeleev's periodic table (1869)

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1913: Moseley's demonstration of the role of atomic number

- In 1913, Moseley showed that the number of protons in the nucleus is the determining factor in the periodic law
- Moseley's work revealed gaps at atomic numbers 43 and 61 (later filled by technetium and promethium)
- By 1939, there were 91 known elements with uranium (Z=92) having the highest atomic number and element 61 missing

Henry Gwyn Jeffreys Moseley (1887-1915)

X-ray spectra of the elements, showing the proportionality of frequency with atomic number. [Moseley, Phil. Mag., 1913]

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Transuranics and the missing element 61

1930s → 1940s-1950s → 1960s

1930s: Fermi proposed creating transuranium elements by irradiating uranium with neutrons (the missed the discovery of fission)

1940s-1950s: Seaborg and co-workers synthesized elements 93-103; Seaborg proposed a new row in the periodic table (the actinides) to accommodate these elements

1960s: To further transuranic research, Seaborg advocated construction of a high-flux reactor and radiochemical processing complex at Oak Ridge

Jakob Marinsky (pictured) and Larry Glendenin discovered element 61 (promethium) at ORNL's Graphite Reactor

ORNL scientists separated the missing element 61 from fission products in 1945, completing the lanthanide series

Seaborg's discovery of the transuranics led him to modify the periodic table

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National Laboratory

The 'Island of Stability'

The possibility of an "island of Stability" of super-heavy elements with greatly increased lifetimes was originally postulated by Seaborg

When neutrons and protons completely fill the energy levels of a given nucleus, the nuclear binding is strongest, leading to longer lifetimes

Heaviest stable isotope (Pb-208) has closed nuclear shells for both protons (82) and neutrons (126)

Next "doubly magic" nucleus occurs around Z=114-126 and N=184, the presumed center of the "Island of Stability"

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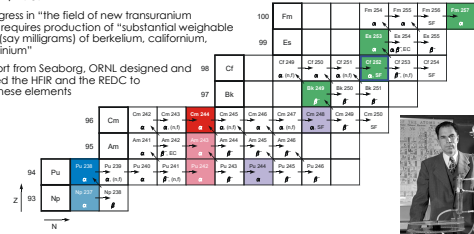


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Realizing Seaborg's vision: A 'very high flux reactor' for heavy element production at ORNL

Letter to AEC Chairman Lewis Strauss,
October 24, 1957

- Future progress in "the field of new transuranium elements" requires production of "substantial weighable quantities (say milligrams) of berkelium, californium, and einsteinium"
- With support from Seaborg, ORNL designed and constructed the HFIR and the REDC to produce these elements



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ORNL's actinide production and research complex

- HFIR** High-power (85-MW) compact core provides intense thermal neutron fluxes in a central flux trap
- REDC** Heavily shielded hot cells for target preparation and processing irradiated materials from HFIR

Isotope production (gram quantities of ²⁵²Cf), neutron scattering, and materials irradiation



Alvin Weinberg,
June 1967

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National Laboratory

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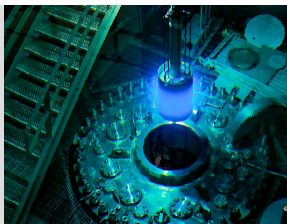
High Flux Isotope Reactor (HFIR) and Radiochemical Engineering Development Center enable heavy element production at Oak Ridge National Laboratory

- HFIR and REDC began operation in 1965 and 1966, respectively
- HFIR operation is expected to continue at least until 2040
- High-end aspects of isotope production (heavy actinides, specially medical isotopes), neutron scattering, and materials irradiation
- Unique capabilities for radiotope separations (>400 isotope shipments annually to universities, hospitals, industry, and other research institutions)

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National Laboratory

HFIR: Unique capabilities

- Highest thermal flux in Western world
 - 2.1×10^{15} n/cm²-s thermal
 - 1×10^{14} n/cm²-s epithermal (< 1 MeV)
 - 4.7×10^{14} n/cm²-s fast (> 1 MeV)
- Brightest cold neutron source in world
- Delivers 6-7 cycles per year
- Missions:
 - Neutron scattering research
 - **Isotope production**
 - Material irradiation
 - Neutron activation analyses

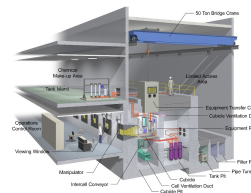


HFIR operations are supported by the Office of Basic Energy Sciences in DOE's Office of Science

11

Radiochemical Engineering Development Center (REDC) Unique capabilities for radiochemical processing and related R&D

- Heavily shielded hot cells for radiation control and alpha containment
- Shielded caves for radiochemical processing and R&D
- Glove box labs for final product purification and R&D
- Radiochemical labs for sample preparation and analysis
- Cold labs for chemical makeup, cold testing, and target fabrication



REDC is fully utilized for research and production for industrial, medical, and research partners

OAK RIDGE
National Laboratory

Remote Cm target fabrication at REDC

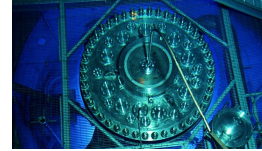
- 35 pellets per target
- Maximum 10 g actinides per target
- Maximum allowable heat flux $1.24 \times 10^6 \text{ Btu}\cdot\text{h}^{-1}\cdot\text{ft}^{-2}$
- Remote welding, hydrostatic compression, shroud installation
- Remote QA inspection
 - | Radiography (pre- and post-compression)
 - | He leak tested to $<1.0 \times 10^{-8} \text{ std}\cdot\text{cc/s}$



OAK RIDGE NATIONAL LABORATORY
ORNL-2014-001

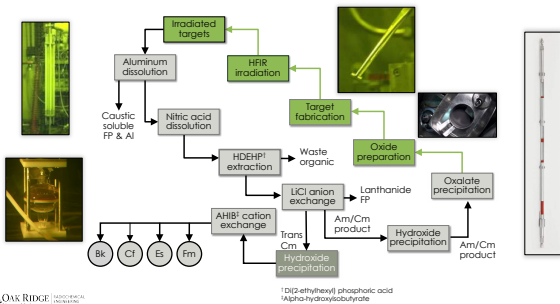
High Flux Isotope Reactor irradiation

- Nine irradiation cycles (250 days) over 18 months
- 90 days for target cooling to allow decay of ^{131}I
- ~240 mg of ^{252}Cf and ~24 mg of ^{249}Bk contained in seven targets



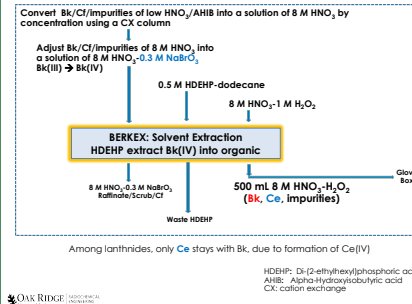
OAK RIDGE NATIONAL LABORATORY
ORNL-2014-001

Irradiated Cm target processing at REDC

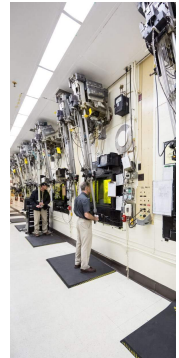


OAK RIDGE NATIONAL LABORATORY
ORNL-2014-001

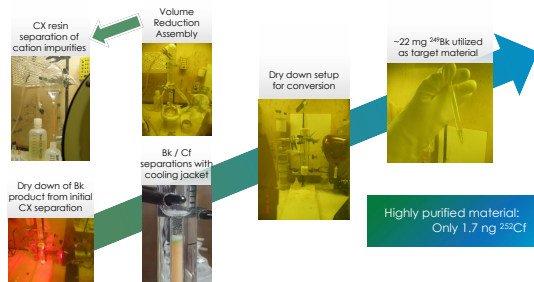
Bk finishing operations – in hot cells



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ORNL-2014-001



^{249}Bk purification process in glove box



OAK RIDGE NATIONAL LABORATORY
ORNL-2014-001

Super-heavy element discoveries enabled by ORNL-produced materials and isotopes

Element	104	105	106	113	114	115	116	117	118
	Rutherfordium	Dubnium	Seaborgium	Nihonium	Flerovium	Moscovium	Livermorium	Tennessee	Oganesson
Year produced	1964	1970	1974	2004	2000	2004	2005	2010	2006
Target	^{249}Pu , ^{249}Cf	^{249}Bk , ^{249}Cf	^{249}Cf	^{243}Am (decay from 115)	^{244}Pu	^{243}Am	^{243}Am , ^{243}Cm	^{249}Bk	^{249}Cf



OAK RIDGE NATIONAL LABORATORY
ORNL-2014-001

Question and answer session

Q: So you are currently developing the production of Lu-177 by indirect method?

A: Lu-177 and the production method is not in my field. Miguel, could you please explain this point?

A: (Miguel) Not if I understand correctly.

Q: In the second or third slide, you also manufacture Ac-225 by proton irradiation. Does your laboratory also process the proton irradiation process for Th-232?

A: We do not do proton irradiation process processing. We work in the so-called TRI-LAB. Targets are irradiated at either Brookhaven National Laboratory or Los Angeles Special Institute. The targets are then separated and purified at Oak Ridge.

Q: So you are just producing Ac-225 from the decay of Th-229?

A: Yes, that is what we do with respect to one facility, and we do it at the other facility. We process targets that have been exposed to accelerator radiation at another national lab.

2.20 K. Ishida (Kyoto Univ.)

Nuclear magnetic resonance in uranium compound superconductors

U-based Ferromagnetic Superconductors

3rd March 2023 1
Kumatori Workshop

K. Kinjo, G. Nakamine, M. Manago, T. Hattori, S. Kitagawa, **K. Ishida**,
Y. Tokunaga^A, H. Sakai^A, S. Kambe^A, N. K. Sato^B, K. Deguchi^B
T. Yamamura^C, Y. Shimizu^C, A. Nakamura^C, D. Li^C, Y. Homma^C, F. Honda^C, D. Aoki^C
Kyoto Univ., ^AASRC, Japan Atomic Agency, ^BNagoya Univ., ^CIMR, Tohoku Univ.

Kyoto Univ.
G. Nakamine, K. Kinjo, M. Manago, S. Kitagawa, T. Hattori, H. Sakai, Y. Tokunaga, S. Kambe

Nagoya Univ.
N. K. Sato, K. Deguchi, T. Yamamura, Y. Shimizu, A. Nakamura, Y. Homma, D. X. Li, F. Honda, D. Aoki

Tohoku Univ. (IMR)

U-based Ferromagnetic Superconductors

	UGe ₂	URhGe	UCoGe	UTe ₂
<i>T</i> _{Curie} (K)	52	9.5	~3	PM
<i>M</i> ₀ (μ _B)	1.48	0.4	0.05	—
Easy Axis	<i>a</i>	<i>c</i>	<i>c</i>	<i>a</i>
<i>P</i> _{SC} (GPa)	~1.2	0 Ambient	0 Ambient	0 Ambient
<i>T</i> _{SC} (K)	0.8	0.26	0.7	1.65

S. S. Saxena *Nature* 406, 587 (2003)
D. Aoki *et al.*, *Nature* 413, 613 (2001)
N. T. Huy *et al.*, *PRL* 99, 067006 (2007)
S. Ran *et al.*, *Science* 365, 684-687 (2019)

Summary of ⁵⁹Co-NQR on UCoGe (Zero field)

T. Ohta *et al.* JPSJ 79, 023707 (2010) Collaboration with N. K. Sato Group

c.f. reference: YCoGe (*P*_{am} with similar lattice constant.)
Y: [Kr] 4d¹5s²
U: [Rn] 5f³, 6d¹7s²
YCoGe_γ = 6.6 mJ/mol K²

No SC & FM down to 100 mK
⇒ SC and FM originate from U-5f electrons
Karube *J. Phys. Soc. Jpn.* 80, 064711 (2011)

Suppression of Superconductivity by Magnetic Field

Orbital-departing Effect
 $H_{c2}^{orb}(0K) = -0.73T_c \frac{dH_{c2}}{dT} \Big|_{T=T_c}$
Second-Order Transition (SOT)

Pauli-departing Effect
First-Order Transition (FOT)
 $H_{c2}^p(0K) = \frac{\Delta(0)}{\sqrt{2}\mu_B}$
Zeeman energy > SC energy

Interesting Properties of FM SC

Case II **H-boosted Superconductivity**
D. Aoki and J. Flouquet: *J. Phys. Soc. Jpn.* 83, 061011 (2014)

URhGe: Reentrant SC was reported in 8 T < μ₀H < 14 T.
UCoGe: SC becomes robust in 5 T < μ₀H < 13 T.
The similar enhancement is also observed in UTe₂

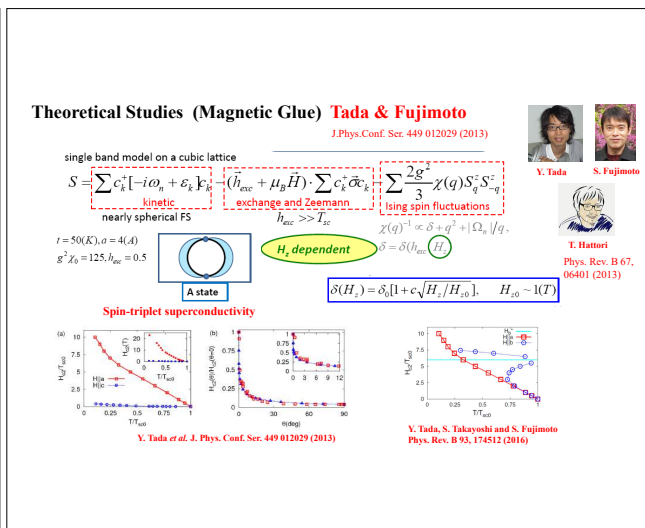
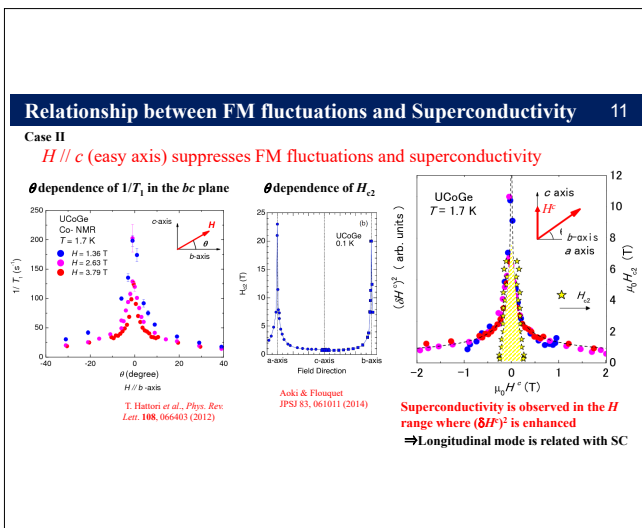
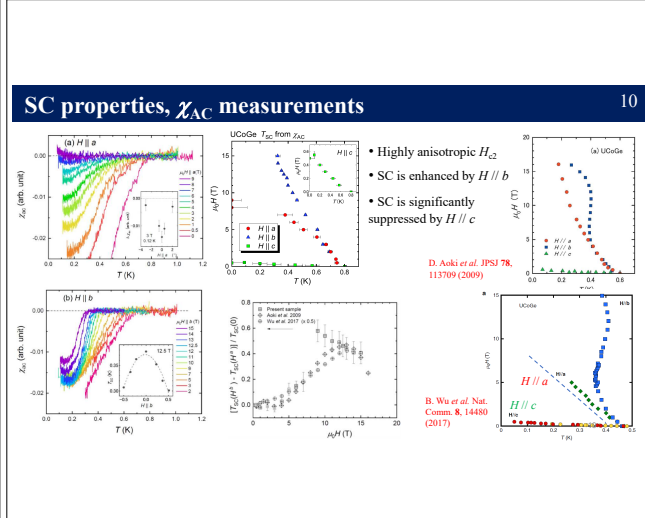
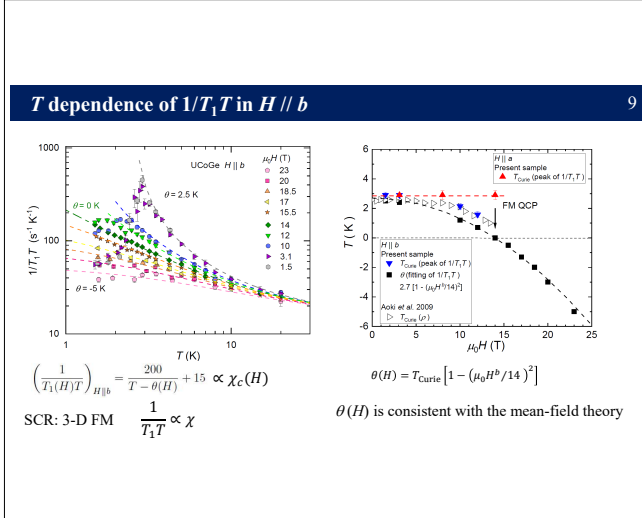
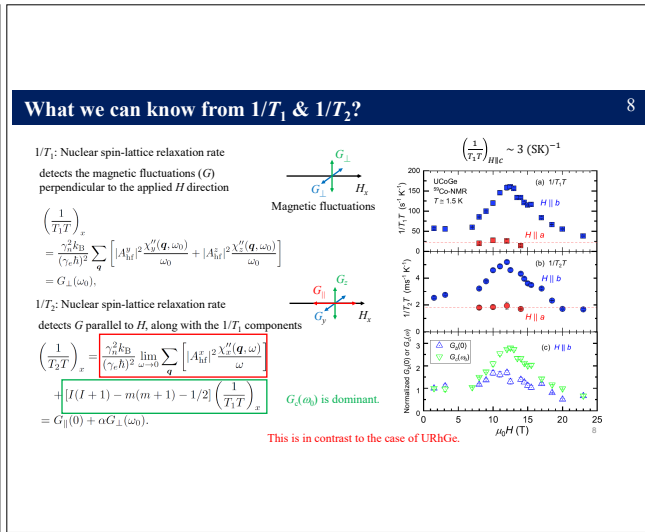
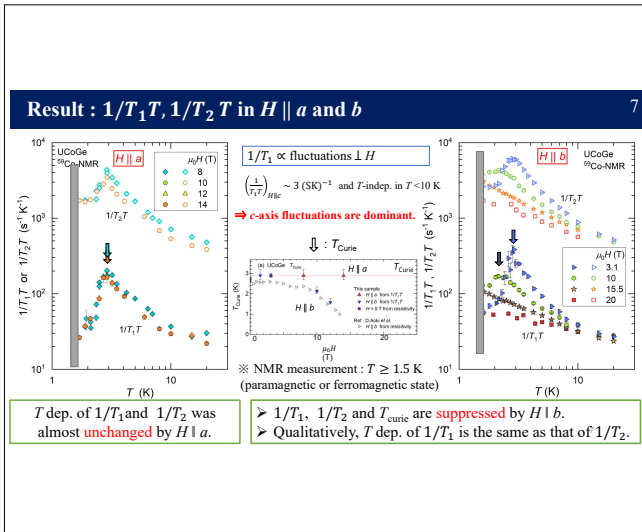
D. Aoki *et al.*, *J. Phys. Soc. Jpn.* 78, 113709 (2009)

Experimental

- ✓ Higher quality sample by D. Aoki *et al.* (RRR ≈ 96)
- ✓ Sample direction is controlled by uniaxial rotation probe.

NMR measurement
✓ We measured 1/*T*₁ and 1/*T*₂ in high field along the *b*-axis and *a*-axis.
✓ We use cryogen-free 25 T magnet @IMR Tohoku Univ.

χ_{ac} measurement for T_{SC}
✓ We measured *T*-dependence of χ_{ac} in fields along the *b*-axis and *a*-axis.
✓ We use the rotation device with piezo which can be used in dilution refrigerator.



Triplet pairing by spin-fluctuation exchange

13

V. P. Mineev *Physics-LiqMetals* 49 (2) 121-148 (2017)

Pairing interaction: "the attraction of one electron by the magnetic polarization cloud of the other" ← **electron - magnon interaction**

$$H_{\text{em}} = -\frac{1}{2}\mu_B^2 t^2 \int d^3r d^3r' S_i(r) \chi_{ij}(r-r') S_j(r')$$

$S(r)$: operator of the electron spin density
 $\chi_{ij}(r)$: medium susceptibility
 t : exchange constant



V. P. Mineev

Pairs of electrons in a ferromagnetic metals occurs in an anisotropic medium due to polarization of the electron liquid and the localized moments.

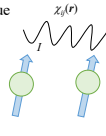
Following the BCS formalism and introducing the physical properties,

$$T_{\text{sc}} = \epsilon \exp\left(-\frac{1+\lambda}{\langle N_0(\mathbf{k})\chi_{zz}^{\text{eff}} \rangle T^2}\right)$$

ϵ : cut-off energy for the pairing interaction
 $1+\lambda$: effective mass renormalization
 $N_0(\mathbf{k})$: density of electronic states on the FS.
 χ_{zz} : z-component of static susceptibility

V. P. Mineev, *PRB* 103, 144508 (2021)

χ_{zz} is the main source of the critical temperature dependence in the magnetic field.



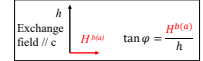
13

Application (1) : T_{SC} enhancement by $H // b$

14

In $H // b$ (a),

$$T_{\text{SC}} \sim \exp\left(-\frac{1}{\left[\langle N_0(\mathbf{k})\chi_c(H^{b(a)}) \rangle \cos^2 \varphi + \langle N_0(\mathbf{k})\chi_b(H^{b(a)}) \rangle \sin^2 \varphi\right] T^2}\right)$$



In UCoGe, $\chi_c \gg \chi_b$ and $h \gg H^{b(a)}$

we simply assume

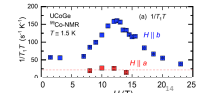
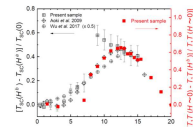
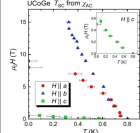
$$T_{\text{SC}}(H^{b(a)}) \sim \exp\left(-\frac{\alpha_1}{\chi_c(H^{b(a)})}\right)$$

$$\frac{T_{\text{SC}}(H^b) - T_{\text{SC}}(H^a)}{T_{\text{SC}}(0)} \sim \exp\left(-\frac{\alpha_2}{\chi_c(H^b)}\right) - \exp\left(-\frac{\alpha_2}{\chi_c(H^a)}\right)$$

$$\propto \alpha_1 \left[\frac{1}{\chi_c(0)} - \frac{1}{\chi_c(H^b)} \right] \propto \frac{T_1(0)T - T_1(H^b)T}{T_1(0)T}$$

, where we use the relation of

$$\chi_c(H) \propto (T_1(H)T)^{-1}$$



Application (2) : T_{SC} sudden suppression by $H // c$

15

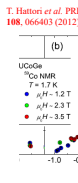
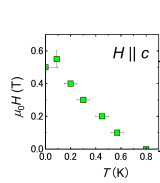
SC is significantly suppressed by $H // c$

In $H // c$,

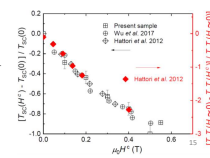
$$T_{\text{SC}}(H^c) \sim \exp\left(-\frac{\alpha_2}{\chi_c(H^c)}\right)$$

$$\frac{T_{\text{SC}}(H^c) - T_{\text{SC}}(0)}{T_{\text{SC}}(0)} \sim \frac{\exp\left(-\frac{\alpha_2}{\chi_c(H^c)}\right) - \exp\left(-\frac{\alpha_2}{\chi_c(0)}\right)}{\exp\left(-\frac{\alpha_2}{\chi_c(0)}\right)}$$

$$\propto \frac{1}{\chi_c(0)} - \frac{1}{\chi_c(H^c)} \propto \frac{T_1(0)T - T_1(H^c)T}{T_1(0)T}$$



$$\chi_c(H^c) \propto (T_1(H^c)T)^{-1}$$



T. Hattori et al. *PRL* 108, 066403 (2012)

UCoGe
 $T_c = 1.7$ K
 $\mu_0 H = 1.2$ T
 $\mu_0 H = 2.0$ T
 $\mu_0 H = 3.5$ T

Reentrant Superconductivity in URhGe

16



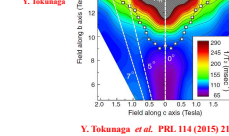
A. Huxley

F. Levy and A. Huxley et al. *Science* 309, 1343 (2005)

$$(1/T_2)_c \propto (\delta H_b)^2$$

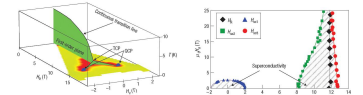


Y. Tokunaga

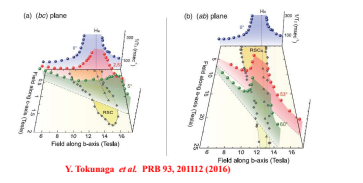


Y. Tokunaga et al. *PRL* 114 (2015) 216401

F. Levy and A. Huxley et al. *Nat. Phys.* 3, 460 (2007)



Relationship between critical fluctuations and SC



Y. Tokunaga et al. *PRB* 93, 201112 (2016)

Summary

17

In FM superconductors UCoGe & URhGe,

- 1) Superconductivity occurs in the FM region ⇒ Microscopic coexistence of FM and SC
- 2) Ising-type FM fluctuations develop at low T ⇒ Longitudinal (c -axis) mode of the moments
- 3) The FM fluctuations controlled by H are coupled with superconductivity.
 ⇒ The Ising-type FM fluctuations induces the spin-triplet superconductivity

• Magnetic-fluctuation mediated unconventional SC

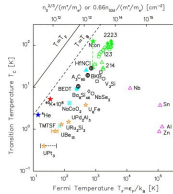


P. Monthoux et al. *Nature* 450, 1177 (2007)



$$T_{\text{sc}} = \epsilon \exp\left(-\frac{1+\lambda}{\langle N_0(\mathbf{k})\chi_{zz}^{\text{eff}} \rangle T^2}\right)$$

V. P. Mineev, *PRB* 103, 144508 (2021)



Y. J. Uemura, *JPCM* 16, S4515 (2004)

cf. BCS (Conventional) superconductor

electron-phonon interaction



$$k_B T_c = 1.14 \hbar \omega_D \exp\left[-\frac{1}{N(E_F)V}\right]$$

spin-triplet SC UTe_2

Question and answer session

Q: You explain superconductivity by linking it to this magnetic fluctuation, but you think that even in UCoGe, in magnetic field B, it is similar to a certain type of magnetic instability possible in URhGe.

A: This is a phase diagram of magnetic properties. You said that if the magnetic field is parallel to the b axis, the ferromagnetism would taper like this, but it doesn't exhibit that behavior. So the different behavior of connectivity A and B is due to the difference in the magnetic dependence of the thermomagnetic properties. But I don't know why the magnetic dependence is so different between the A and B axes.

Q: But anyway, there seems to be a similarity between UCoGe and URhGe.

A: It is more localized in URhGe, but as you know these are system compounds and magnetic structures, but it could be as different as that.27 min

Q: How do you think this calculation is valid for unknowns?

A: That is the most difficult part of the calculation.

Q: The heat capacity deviates slightly from the adapted value.



A: I imagine that if we can use the results of this calculation as input for CALPHAD. Is this concept okay?

Q: Yes, it is okay.

A: Thank you.

2.21 H. Shishido (Tohoku Univ.)

First-principles calculations for CALPHAD calculations of minor actinide fuels

First-principles calculations for CALPHAD calculations of minor actinides fuels

Hiroki Shishido
Department of Quantum Energy Engineering,
Graduate School of Engineering,
Tohoku University

1

1. Introduction

1.1 Severe problems on fusion reactor development

Controlled fusion reaction will be achieved by the ITER project.

↓

Demo design is not fixed due to remaining engineering issues

- 1) the divertor system loaded by extremely high heat flux
- 2) maintenance of components loaded by neutrons

Even after the Demo construction, , ,

DEMO reactors

→

Commercial reactors

The power increase brings **more severe heat load** to the divertor.

As one of the options,
Transmutation of minor actinides (MA) and fission product generated from nuclear power plants.

2

[1] <https://www.iter.org/>

1. Introduction

1.2 Closed nuclear fuel cycle with a fusion reactor [2]

Copyright protected image

[2] H. Hashizume et al., presented at the 14th International Symposium on Fusion Nuclear Technology, 2019 Budapest, Hungary.

3

1. Introduction

1.3 MA transmutation in a fusion reactor

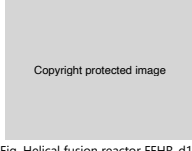


Fig. Helical fusion reactor FFHR-d1^[3]

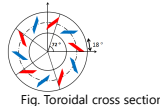


Fig. Toroidal cross section




Fig. Poloidal cross section

Copyright protected image

[3] A. Sagara et al., Fusion Engineering and Design 89 (2014) 2114-2120.
[4] Y. Furudate, H. Shishido et al., Prog. Nucl. Energy 103 (2008) 28.

4

1. Introduction

1.4 Pu transmuted from MA

Copyright protected image

[7] A. Sasahara et al., Journal of Nuclear Science and Technology 41 (2004) 448-456.

5

1. Introduction

1.4 Pu transmuted from MA (Cont'd)

Conventional cycle
 Power generation
 Pu? Fast reactor
 Pu? LWR
 Fuel production → U, Pu → Reprocessing → MA, FP → Separation → Fuel production

New additional cycle
 Transmutation cycle
 Fusion reactor → Blanket material production → Long-lived FP → Separation → Fuel production
 MA, FP → Separation → MA → Fusion reactor

Other FP → Storage (detoxified soon)

Pu

Is it possible to re-utilize the transmuted Pu in a fission reactor?
High level **waste** → Energy **resource**?

6

1. Introduction

1.5 Transmuted Pu in a fast reactor



Fig. Radial core layout[8]

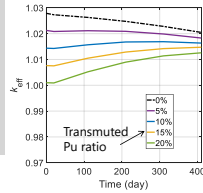


Table Comparison of Pu isotope ratio

	²³⁸ Pu	²³⁹ Pu	²⁴⁰ Pu	²⁴¹ Pu	²⁴² Pu
MOX fuel	2.2	59.5	26.7	3.9	7.6
Pu transmuted from MA	82.2	4.8	2.6	0.6	10.0

Possibility to maintain a constant level of k_{eff} during operation

[8] OECD/NEA, NEA/NSC/R(2015)9, (2016).

7

1. Introduction

- Development of fuel containing only MA for transmutation systems—(Np, Am, Cm)O₂.
- First, we have considered conducting a numerical analysis using the CALPHAD method to evaluate the phase diagram.
- Since thermodynamic quantities are required as inputs to CALPHAD, we have worked on the predictive evaluation of these quantities by first-principles calculations.

8

2. Today's presentation contents

The presentation provides:

- 1) Density functional theory (DFT) based electronic structure calculations for UO₂, AmO₂, and NpAmO₂
 - ❑ Structure optimization
 - ❑ Density of states
- 2) Phonon calculations based on the DFT calculation
 - ❑ Free energy
 - ❑ Heat capacity at constant pressure

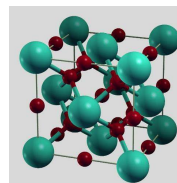
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3. Materials and methods

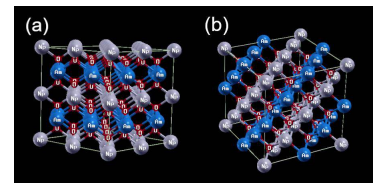
3.1 DFT simulation

Materials UO₂, AmO₂, NpAmO₂

Calculation cell



UO₂, AmO₂
(Fm-3m)



NpAmO₂ (a) P4/mmm, (b) R-3m

10

3. Materials and methods

3.1 DFT simulation

WIEN2k^[9]

Density functional theory calculation based on all-electron calculation method

- Exchange–Correlation functional: PBE
- Sampling k points: 1,000
- $R_{MT}K_{max} = 8.5$
- SCF convergence condition: 10^{-5} Ry
- Not considered electron spin polarization

[9] P. Blaha et al., J. Chem. Phys. 152, 074101 (2020).

11

3. Materials and methods

3.2 Phonon calculation

Phonopy^[10]

Thermal properties (free energy, heat capacity, and entropy) related to phonon in solids are calculated using DFT calculation results

Quasi harmonic approximation^[11]

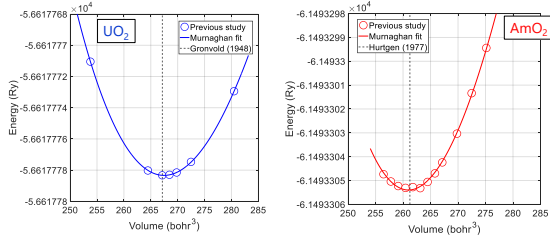


[10] A. Togo, J. Phys. Soc. Jpn. 92, 012001 (2023). [11] K. Toyoura, J. MMIJ 129, 270-277 (2013).

4. Electronic structure calculation

4.1 Structure optimization— UO_2 and AmO_2

Energy–volume curve



- [12] F. Gronvold *et al.*, *Nature* 162, 69-70 (1948).
 [13] F. D. Murnaghan, *Proc. Natl. Acad. Sci. USA*, 30, 244-247 (1944).
 [14] C. Hurltgen *et al.*, *Inorg. Nucl. Chem. Lett.* 13, 179-188 (1977).

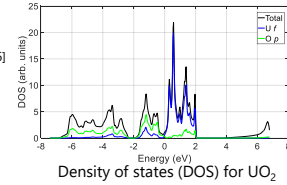
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4. Electronic structure calculation

4.2 Density of states— UO_2

Experiment
 UO_2 band gap
 = 2.00–2.50 eV^[15, 16]

GGA+U^[17] or TB-mBJ^[18]
 were employed ...
 band gap ≤ 0.5 eV



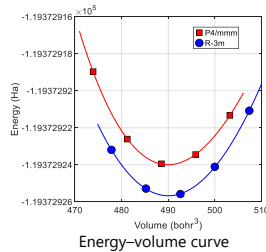
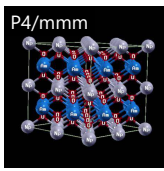
The calculation conditions need to be reviewed for accurate evaluation of the electronic state.

- [15] T.T. Meek *et al.*, *Mater. Lett.* 59, 1085-1088 (2005).
 [16] S.W. Yu *et al.*, *Phys. Rev. B* 83, 165102 (2011).
 [17] A.I. Liechtenstein *et al.*, *Phys. Rev. B* 52, R5467-R5470 (1995).
 [18] D. Koller *et al.*, *Phys. Rev. B* 85, 155109 (2012).

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4. Electronic structure calculation

4.3 Structure optimization— NpAmO_2

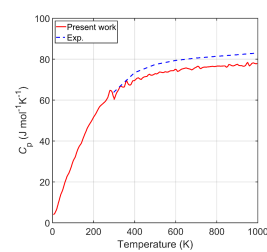
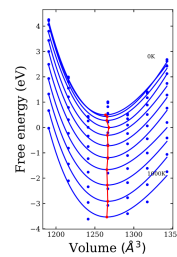


NpAmO_2 mixture R_3m is more stable?

15

5. Phonon calculations

5.1 Thermal properties— UO_2



The E–V curves were rattled because of the loose convergence determination of the DFT calculations.

- [19] IAEA, *Thermodynamic database for nuclear fuels and reactor materials*.

16

6. Summary

- Density functional theory (DFT) calculations
 - ✓ The results of structural optimization correspond to the experimental results.
 - ✓ Applying GGA+U and TB-mBJ did not improve the band gap underestimation.
 - ✓ Since there are some problems specific to the all-electron method, it is necessary to review the calculation conditions in the future.
- Phonon calculations based on the DFT calculation
 - ✓ Although only UO_2 was implemented, it was confirmed that the heat capacity can be generally evaluated.

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Question and answer session

Q: How do you think this calculation is valid for unknowns?

A: That is the most difficult part of the calculation.

Q: The heat capacity deviates slightly from the adapted value.

A: I imagine that if we can use the results of this calculation as input for CALPHAD. Is this concept okay?

Q: Yes, it is okay.

A: Thank you.

2.22 M. Abe (Hiroshima Univ.)

Development of relativistic electron correlation program for calculation of actinide compounds

2022年度
「アクチノイドの物性化学と応用・原子炉照射医療用RI製造に関する専門研究会」
2023年3月2, 3日 京都大学原子力複合研究所・オンライン

アクチノイド化合物計算に向けた 相対論的電子相関プログラム開発

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

広大： 阿部稜里・野田紘平・増田康人
都立大：波田雅彦・中谷直輝・吉田均・佐藤有汰留・岩室寿美果

アクチノイド化合物をターゲットとする背景

福島第一原発事故による放射性廃棄物

燃料成分 (UO₂)
燃料被覆管 (Zr)
制御棒材料
原子炉構造材料
海水の注水

燃料デブリ
アクチノイド化合物の混合物

実験研究による燃料デブリの性質解明の難しさ

高い研究コスト	安全性確保が困難
測定の難しさ	研究施設の不足

理論計算によるアクチノイド化合物の 化学的・物理的性質の解明への期待

[1] JAEA "Characterization of fuel debris" <https://www.jaea.go.jp/english/04/ntokai/fukushima>

アクチノイド化合物の理論計算における問題点①

電子相関理論について

軌道が離散的
→ 1つの電子配置が重要

単参照電子相関理論

軌道が(擬)縮退
→ 複数の電子配置が重要

多参照電子相関理論

アクチノイド原子：d軌道やf軌道が擬縮退
→ 多参照電子相関理論が必要
(例) CASPT2, MRCI, MRCC

アクチノイド化合物の理論計算における問題点②

アクチノイドの原子番号：Z = 89 ~ 103 (重元素)

× 非相対論
× 低精度相対論法
○ 2成分近似法 (高精度)
→ 高精度相対論法が必要

多参照電子相関理論と高精度相対論法を
同時に取り扱える実用的なプログラムの開発を実施

[2] J Seino et al, Chem. Phys. Lett. 461, 2008, 327-331

理論① 多参照電子相関理論 CASPT2法

二次空間

完全活性空間 (CAS)
 $C_1 \begin{pmatrix} \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \end{pmatrix} + C_2 \begin{pmatrix} \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \end{pmatrix} + C_3 \begin{pmatrix} \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \end{pmatrix} + \dots + C_N \begin{pmatrix} \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \end{pmatrix}$

不活性空間
 $\Phi_1, \Phi_2, \Phi_3, \Phi_N$

CASCI法

$|0\rangle = \sum_i C_i |\Phi_i\rangle$ CAS内で取りうる全ての電子配置に対して、線形結合をとり、配置係数Cを変分的に決定

CASPT2法

0次波動関数 $|0\rangle$ からさらに1,2電子励起した配置を摂動的に考慮する方法

理論② 4成分法と厳密2成分法の比較

4成分Dirac法 $H_4^{\text{Dirac}} \Psi_4 = E \Psi_4$ $\xrightarrow{\text{ユニタリー変換}} H_2^+ \Psi_2 = E^+ \Psi_2$ (厳密2成分法)

$$U^\dagger H_4 U \approx \begin{pmatrix} H_2^+ & 0 \\ 0 & H_2^- \end{pmatrix}$$

	4成分Dirac法	厳密2成分法(X2C法)
得られる解	電子解と陽電子解	電子解
計算コスト	高い	低い
計算の正確性	高い	4成分法とほぼ同等

厳密2成分法：精度を落とさずに低コストで計算可能

[3] M Hayami et al, J. Chem. Com. 39, 27, 2333

量子化学計算プログラムの比較

7

	DIRAC	UTChem	MOLCAS	Gaussian
4成分Dirac法	○	○	×	×
厳密2成分法	○	×	△	×
CASCI(CASSCF)	×	○	○	△
CASPT2	×	○	○	×

DIRACに基づく
CASCI/CASPT2
計算法の確立

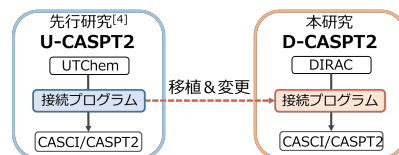
厳密2成分法
+
多参照電子相関法

アクチノイド
化合物への適応
が可能になる

本研究の目的と方法

8

アクチノイド化合物の計算を可能とする
DIRACに基づくCASCI/CASPT2プログラム(D-CASPT2)の確立



研究内容

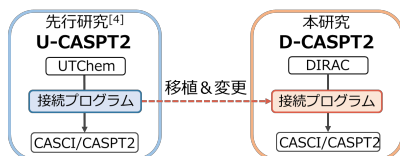
- (1) UTChemとDIRACを比較, 接続プログラムを移植・変更 (2電子積分の冗長性の除去, 対称性の拡張など)
- (2) 機能の拡張 (IVO法の適用)

[4] M Abe et al, J. Chem. Phys. 2006, 125, 234110

本研究の目的と方法

9

アクチノイド化合物の計算を可能とする
DIRACに基づくCASCI/CASPT2プログラム(D-CASPT2)の確立



研究内容

- (1) UTChemとDIRACを比較, 接続プログラムを移植・変更 (2電子積分の冗長性の除去, 対称性の拡張など)
- (2) 機能の拡張 (IVO法の適用)

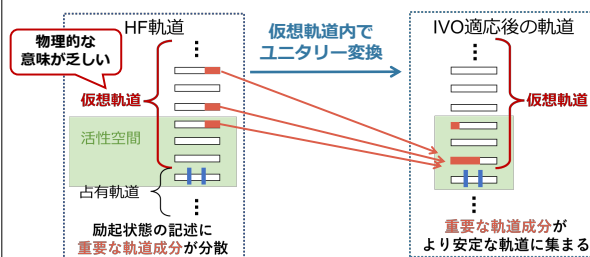
[4] M Abe et al, J. Chem. Phys. 2006, 125, 234110

(2)機能の拡張 IVO (Improved Virtual Orbital) 法

10

CASSCF法は計算コストが高い → 参照関数: IVO-CASCI法

IVO(Improved Virtual Orbital)法^[5]
基底状態のHOMOから1電子励起した状態に対して
より最適な軌道を生成することで仮想軌道の記述を改善



[5] S Huzinaga, J. Chem. Phys. 1971, 54, 1948-1951

計算の詳細

11

- ・プログラム DIRAC22
実装したCASCI/CASPT2およびRASCI/RASPT2
 - ・ハミルトニアン: X2C (厳密2成分相対論法)
4成分Dirac (4成分相対論法)
- ①プログラム動作の確認
 - ・U-CASPT2とD-CASPT2の比較 (N₂, NO, H₂O)
 - ・C_s, C₁に対する計算の実装 (メタノール, 非対称CH₄)
 - ・厳密2成分法の適応 (UO₂²⁺)
 - ・IVO法を適応し, 分光定数を計算 (N₂)
 - ②アクチノイド化合物の計算への応用 (UO₂²⁺)
 - ・MO係数の解析と活性空間の設定
 - ・分光定数 (平衡核間距離, 解離エネルギー)
 - ・ポテンシャル曲線と励起エネルギー

計算の詳細

12

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 - ・ポテンシャル曲線と励起エネルギー

① プログラム動作の検証 (U-CASPT2との比較) 13

先行研究のU-CASPT2と本研究のD-CASPT2の結果を比較

	N ₂ (C _{32h})		NO (C ₃₂)	
	STO-3G, 12スピノール 6電子		STO-3G, 12スピノール 6電子	
	U-CASPT2	D-CASPT2	U-CASPT2	D-CASPT2
HF	-103.04546316	-103.04546311	-127.5470334	-127.5470333
CASCI	-103.05416899	-103.05416893	-127.6558412	-127.6558411
CASPT2	-103.26008134	-103.26008128	-127.8379457	-127.8379456

H ₂ O (C ₂)		U-CASPT2とD-CASPT2 は数値誤差の範囲で 完全に一致
6-31G, 10スピノール 6電子		
	U-CASPT2	D-CASPT2
HF	-74.883904471	-74.883904464
CASCI	-74.884304152	-74.884304146
CASPT2	-75.040813153	-75.040813152

[単位: a.u.]

① プログラム動作の検証 (C_s, C_iに対する計算の実装) 14

U-CASPT2: C_sとC_i対称性の計算は実装されていない。
達成条件: CAS1配置/HF=CASCI, MP2=CASPT2エネルギー

	メタノール (C _s)	非対称CH ₄ (C _i)
	cc-pVDZ, 10スピノール 6電子	STO-3G, 2スピノール 2電子
HF	-111.13616466	-37.460336926
CASCI	-111.13616466	-37.460336926
MP2	-111.55628122	-37.58766131
CASPT2	-111.55628125	-37.58766134

HFとCASCI, MP2とCASPT2エネルギーは
数値誤差の範囲で完全に一致

DIRACに実装されている対称性
C_{32h}, C₃₂, C₂, C_s, C_i に対して
D-CASPT2は正常に作動

① プログラム動作の検証 (厳密2成分法の適応) 15

UO₂²⁺分子のエネルギー計算過程の計算時間

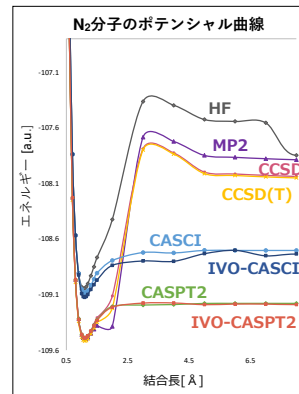
	DIRAC		CASCI/CASPT2		合計
	HF	積分変換 その他	CASCI	CASPT2	
厳密2成分法	20.1	93.0	29.1	94.4	1131.8
4成分 相対論法	657.7	926.0	23.1	89.5	1134.4

[MPI8並列計算, 単位: 秒, U: dyall.c2vz, O: 6-31G+*, 12スピノール 4電子]

厳密2成分法 積分変換部の計算コストが大幅に低下

アクチノイドを含む重原子系の計算を
現実的な時間で計算可能になる

① プログラム動作の検証 (IVO法) N₂分子の分光定数 16



基底関数: dyall.3zp
状態: 基底状態(Ω=0_g)
活性空間: 12スピノール, 6電子

- HF, MP2, CCSD, CCSD(T) は中～長距離で破綻
- IVO-CASPT2が安定したポテンシャル曲線を描画

① プログラム動作の検証 (IVO法) N₂分子の分光定数 17

	R _e [Å]	ω _e [cm ⁻¹]	B _e [cm ⁻¹]	a _e [cm ⁻¹]	D _e [kcal/mol]
CCSD(T)	1.1006	2394.5	1.9878	0.0166	901.6
CASCI	1.0994	2406.8	1.9922	0.0144	240.1
CASPT2	1.0991	2407.8	1.9935	0.0168	196.6
IVO-CASCI	1.0939	2506.2	2.0124	0.0157	213.4
IVO-CASPT2	1.0988	2386.3	1.9943	0.0184	208.0
実験値[6]	1.0977	2358.6	1.9982	0.0173	228.4

R_e: 平衡核間距離(Å)
ω_e: 調和振動数(cm⁻¹)
B_e: 回転定数(cm⁻¹)
a_e: 非調和項(cm⁻¹)
D_e: 解離エネルギー(kcal/mol)

- CASPT2法がすべての数値において、よい計算結果を得ている
- IVO法を適用すると、CASPT2法において、すべての数値が実験値に近づく

→ IVO法の適用は効果あり

[6] <https://webbook.nist.gov/chemistry/form-sect/> NIST Chemistry WebBook

計算の詳細 18

- プログラム DIRAC22
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4成分Dirac (4成分相対論法)

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- U-CASPT2とD-CASPT2の比較 (N₂, NO, H₂O)
- C_s, C_iに対する計算の実装 (メタノール, 非対称CH₄)
- 厳密2成分法の適応 (UO₂²⁺)
- IVO法を適応し、分光定数を計算 (N₂)

② アクチノイド化合物の計算への応用 (UO₂²⁺)

- MO係数の解析と活性空間の設定
- 分光定数 (平衡核間距離, 解離エネルギー)
- ポテンシャル曲線と励起エネルギー

②アクチノイド化合物への応用 (UO_2^{2+} 計算の活性空間) 19
HOMO・LUMO付近の分子軌道の解析 ($R_{\text{U-O}}=1.75 \text{ \AA}$)

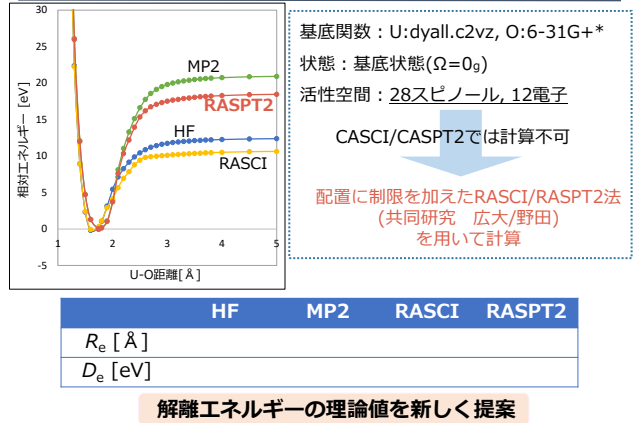
エネルギー [a.u.]	主な軌道の成分
-0.354	U f 50% p 12% O p 36%
-0.377	U f 38% p 20% O p 36%
-0.404	U f 98%
-0.414	U f 90%
-0.414	U d 100%
-0.422	U f 72%
-0.426	U d 87%
-0.427	U f 95%
-0.429	U s 61% (LUMO)
-1.023	U p 37% O s 40% p 21% (HOMO)
-1.024	O p 90% U f 8%
-1.039	O p 52% s 36% U d 12%
-1.046	U p 39% O s 46% p 11%
-1.056	O p 72% U d 26%
-1.059	O p 72% U d 26%
-1.431	U p 53% O s 44% p 2%

U5f,6d由来の軌道が擬縮退

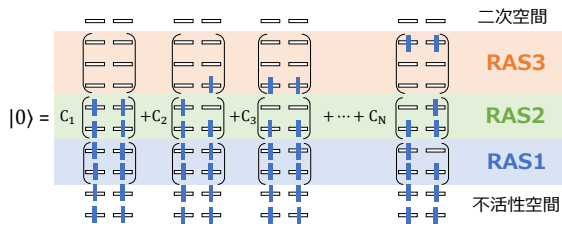
大きな活性空間が必要

UとOの軌道成分が混合

②アクチノイド化合物への応用 (UO_2^{2+} の分光定数) 20

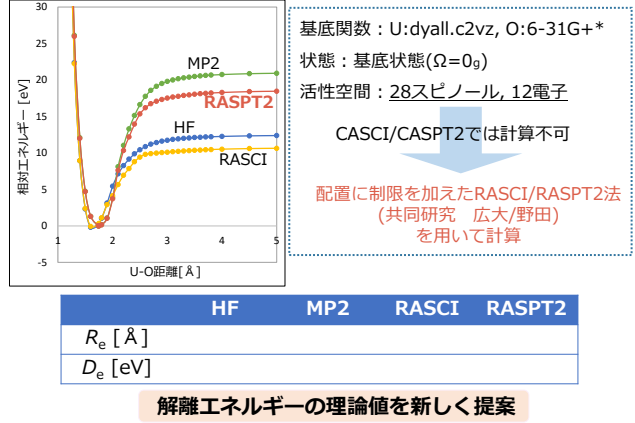


参考: RASCI/RASPT2の実装 (広大・野田) 21



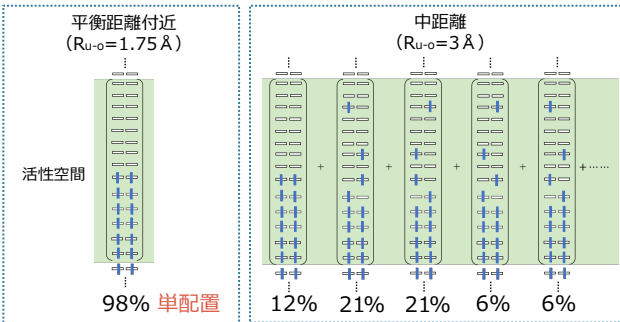
- RASCIの実装
 - CAS空間をRAS1,RAS2,RAS3の3つに分ける
 - RAS1は**ホール**の数を制限
 - RAS2は**制限なし**
 - RAS3は**電子数**を制限
- RASPT2
 - RASCIができればCASPT2を使うだけで実現

②アクチノイド化合物への応用 (UO_2^{2+} の分光定数) 22



②アクチノイド化合物への応用(多参照電子相関理論の必要性) 23

波動関数の解析: 主な電子配置について

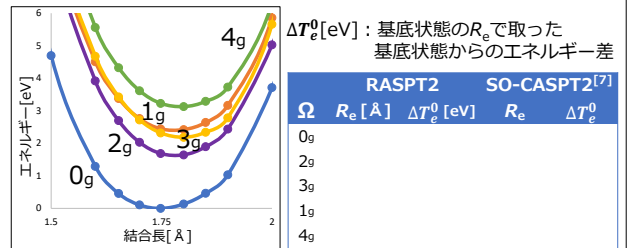


3Å以降の中・長距離では**多配置性**が極めて顕著

多参照電子相関理論の必要性を再確認

②アクチノイド化合物への応用 (UO_2^{2+} の励起エネルギー) 24

$\Omega=0_g$ (基底状態)と $1_g, 2_g, 3_g, 4_g$ (励起状態)に対する計算



先行研究(SO-CASPT2)とRASPT2の比較

励起配置の準位: 定性的に一致

励起エネルギー: 2_g 状態以外はよく一致

→ 基底関数や活性空間の取り方への依存性を今後検討

[7] Pierloot, K.; van Besien, E. J. Chem. Phys. 2005, 123, 204309

相対論的CASPT2プログラム(D-CASPT2)の開発

- ✓ DIRACに実装されている対称性である
C_{32h}、C₃₂、C₂、C_s、C₁へのプログラム適応に成功
- ✓ 厳密2成分法の計算に適応
- ✓ IVO法を適応し、CASPT2法の計算結果を改善

アクチノイド化合物の計算への応用

- ✓ UO₂²⁺の平衡核間距離と解離エネルギーを算出
- ✓ UO₂²⁺のポテンシャル曲線を描画し、励起エネルギーを計算

**本研究で開発したプログラムでアクチノイド分子の
厳密2成分-CASPT2計算が可能となった**

Question and answer session

Q: Taking the UO_2 story as an example, is it better to incorporate all of the orbitals when some are in the form of incorporation?

A: It probably depends on whether the electron configuration you are looking for is in the excited state or the ground state, and what the composition of the excited state is. The fine tuning you point out is necessary.

Q: Because of the cost, if you take out what you don't want and put in orbitals in even different places, wouldn't that improve convergence and lower the energy more and more?

A: Yes, it would.

Q: You were just working on UO_2 . Do you have any such plans to do calculations on this kind of material in the future?

A: I think that we can immediately work on how the basic electronic state and electronic structure will change when we change to an actinide system.

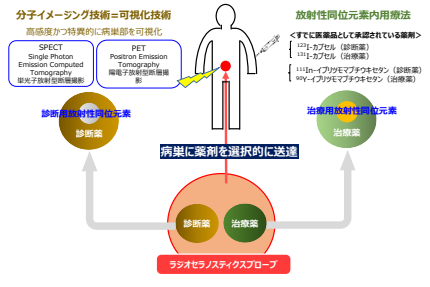
Q: Is it correct to think of changing the actinide atoms in the oxide system?

A: Yes, that is correct.

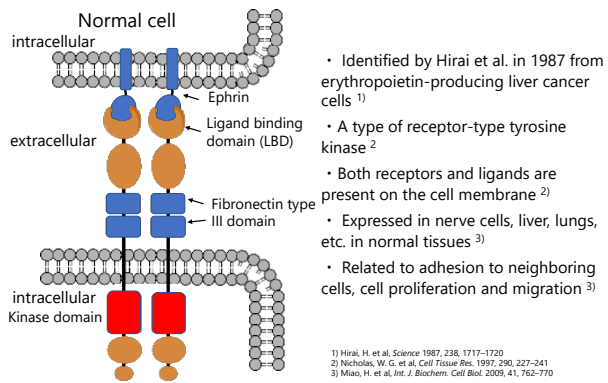
Tumor-targeted radio-ceranostics drug discovery and clinical application

Tumor-targeted radio-theranostics drug discovery and clinical application

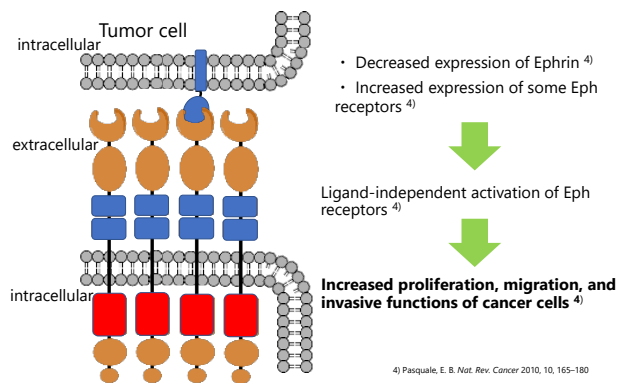
Kyoto Pharmaceutical University
Hiroyuki Kimura



Erythropoietin-producing hepatocellular (Eph) Receptor



Relationship between metastasis, invasion and Eph receptors in cancer cells



Eph receptor A2 (EphA2) and cancer

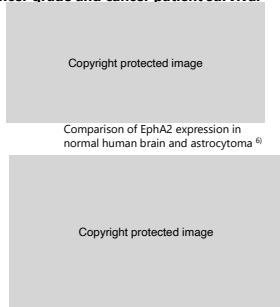
Expressed in various solid tumors



Cancer cell line encyclopediaに登録されているがん細胞におけるEphA2の発現量比較⁵⁾

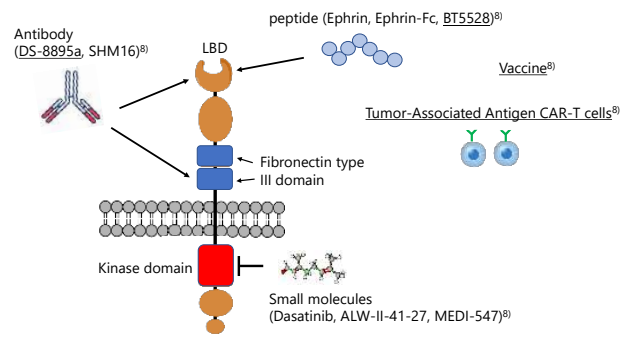
5) Giordano, G. et al. Cells 2021, 10, 2893
6) Zelinski, D. P. et al. Cancer Res. 2001, 61, 2301-2306
7) Nikas, I. et al. Diagnostics 2022, 12, 366

EphA2 expression levels have been linked to cancer grade and cancer patient survival



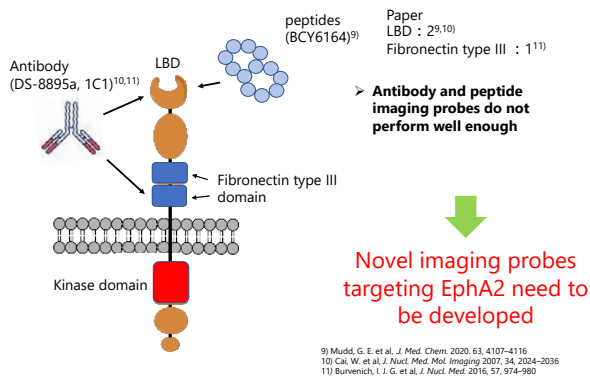
Breast Cancer Patients EphA2 expression level and survival⁷⁾

Current status of therapeutic drug development targeting EphA2

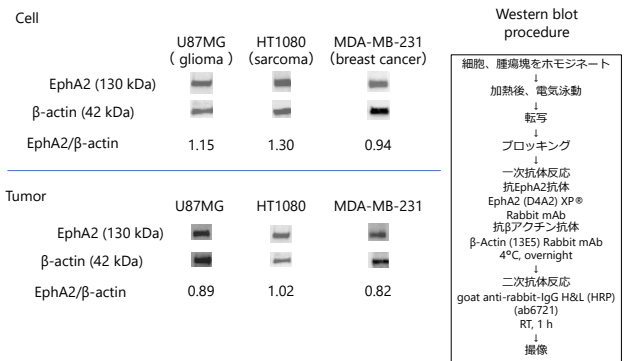


11) Xiao, T. et al. J. Hematol. Oncol. 2020, 13, 113

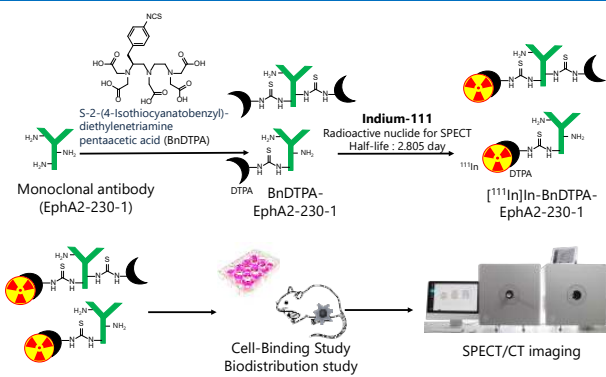
Development Strategy for Imaging Probes Targeting EphA2



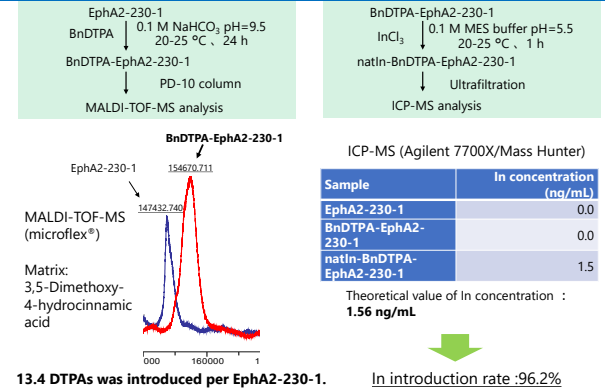
Confirmation of EphA2 expression in cancer cells



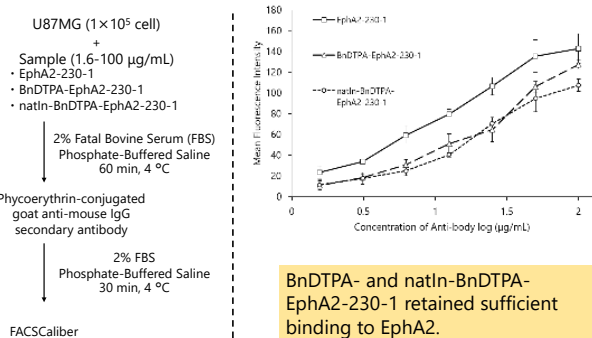
Research Outline



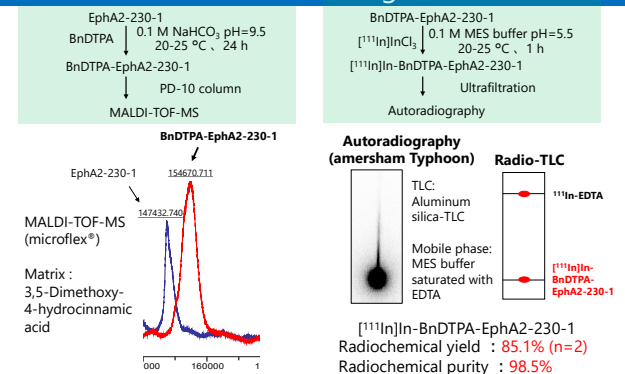
BnDTPA Conjugates with the Antibody



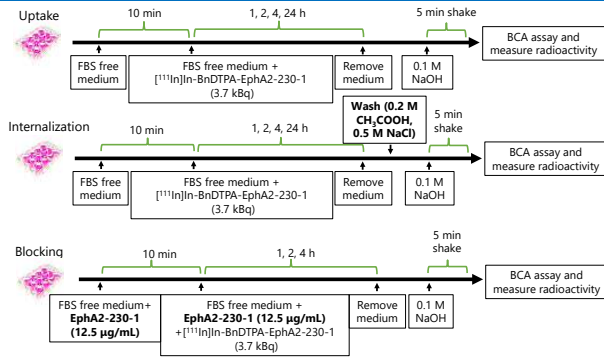
Binding Affinity for EphA2



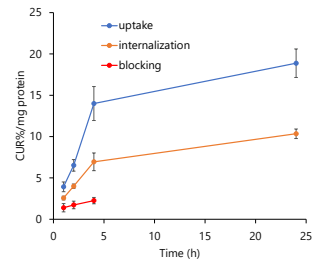
Radiolabeling



Cell-Binding Study (U87MG cell)

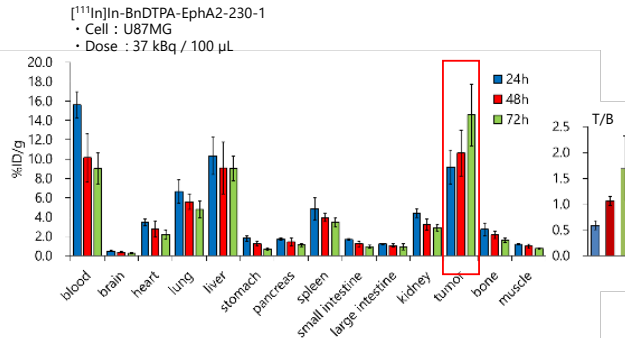


Cell-Binding Study (U87MG cell)



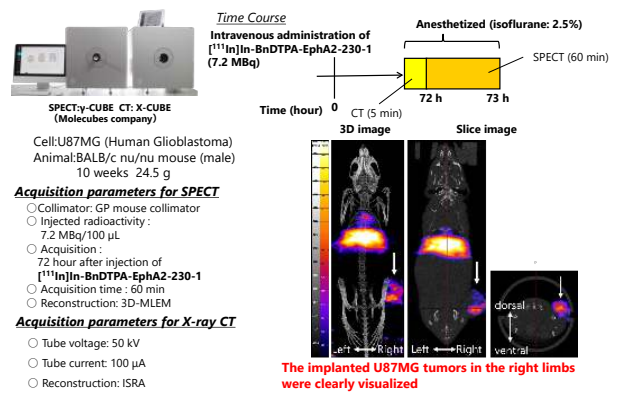
$[^{111}\text{In}]\text{-BnDTPA-EphA2-230-1}$ was shown to be taken up into U87MG cells in a time-dependent manner. On the other hand, $[^{111}\text{In}]\text{-BnDTPA-EphA2-230-1}$ was barely taken up into the cells in the blocking group at 4 h. This cold-target inhibition assay demonstrates that the cellular uptake of $[^{111}\text{In}]\text{-BnDTPA-EphA2-230-1}$ is mediated by EphA2 but not by nonspecific endocytosis in U87MG cells.

Biodistribution of $[^{111}\text{In}]\text{-BnDTPA-EphA2-230-1}$



High uptake of $[^{111}\text{In}]\text{-BnDTPA-EphA2-230-1}$ in the tumor was confirmed and continued to increase for 72 h.

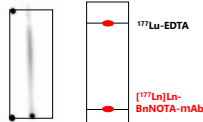
SPECT/CT ($[^{111}\text{In}]\text{-BnDTPA-EphA2-230-1}$)



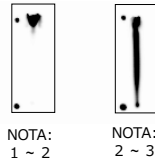
$[^{177}\text{Lu}]\text{Ln-BnNOTA-mAb}$

microtube
 ← 0.3M AcONa 30 μL
 ← NOTA-mAb 25 μL (50 μg)
 ← $^{177}\text{LuCl}_3$ 30 μL (10 MBq)
 <40°C, 1hr>

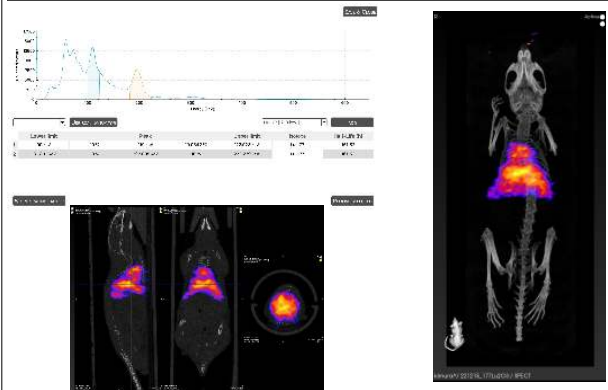
Autoradiography
 (amersham Typhoon) **Radio-TLC**



Radiochemical yield : 88%
 Introduction rate of NOTA : 6 ~ 8



SPECT imaging : $[^{177}\text{Lu}]\text{Ln}_2\text{O}_3$



Question and answer session

Q: Am I correct in understanding that as long as lutetium does not interfere?

A: Yes. But in fact this is labeled because of the number of introductions.

Q: Do you know what causes the slightly lower uptake of indium DTPA?

A: Maybe in this case, the number of indium DTPA is a little high, 13.

Q: When using lutetium, wasn't it DTPA?

A: NOTA.

Q: If we change to NOTA, does the affinity still decrease if the introduction rate of that is high?

A: Even with a similar number of installations, NOTA is more compact and has a higher affinity.

Q: I would like to ask one question from the medical field. Is it possible to make a labeled formulation of gallium-68 instead of indium?

A: Yes. It looks like the formulation is ready. What about zirconium?

A: Zirconium is labeled with defilostamine, so it is ready.


Q: If there seems to be a demand for upgrading with a complexing agent (chelating agent), I would like to try a little.

A: Various ligands are being developed overseas. I would be very interested in any joint research with you.

2.24 M. Suzuki (KURNS, Kyoto Univ.)

Quantum Beam Bio-Systems Analysis and Application Unit

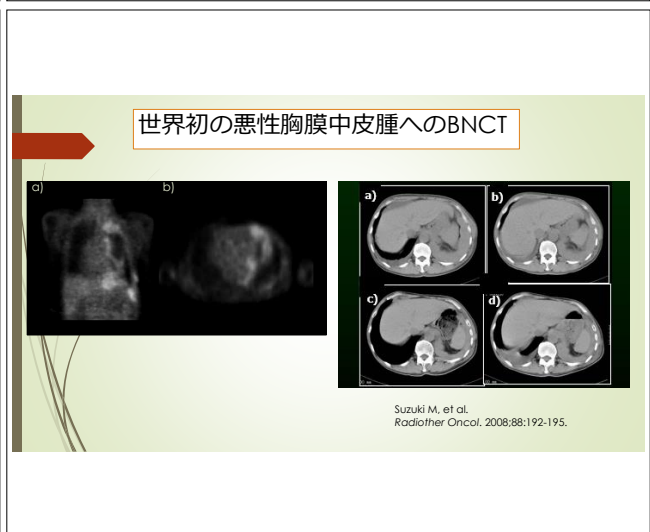
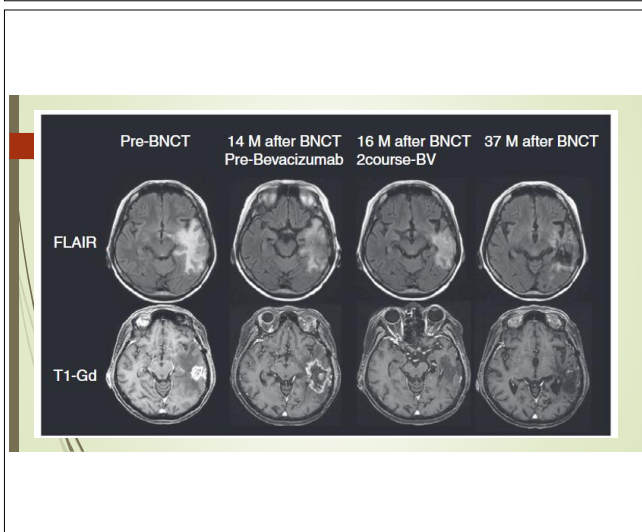
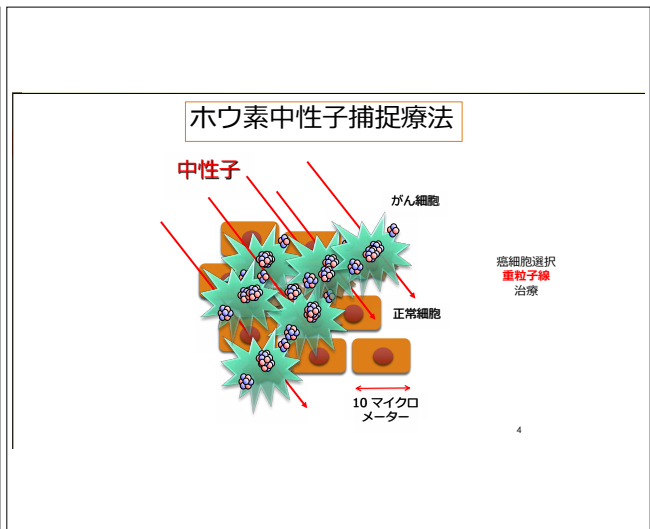
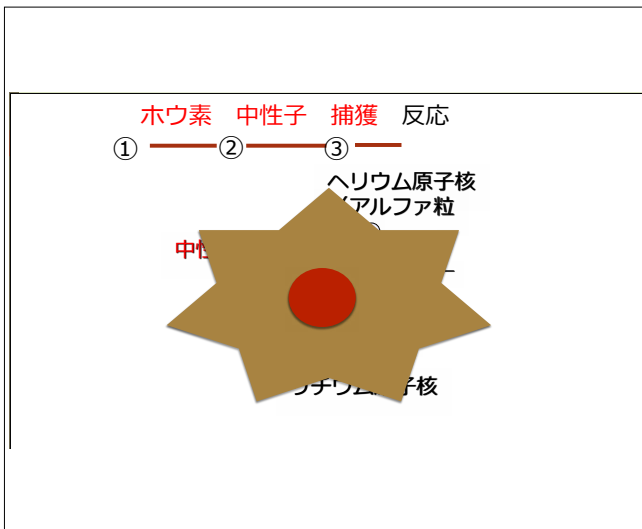
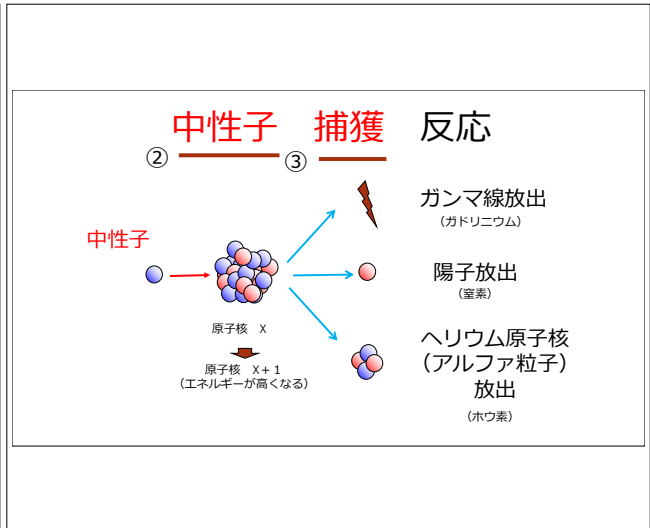
Quantum Beam Bio-Systems Analysis and Application Unit



Minoru Suzuki¹ Yusuke Wada^{1,2}, Takushi Takata¹

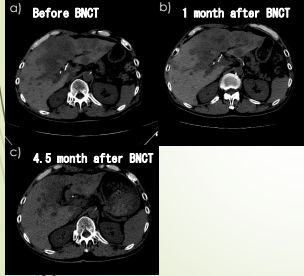
¹ Particle Radiation Oncology Research Center
Institute for Integrated Radiation and Nuclear Science, Kyoto University

² Veterinary Medical Center, School of Veterinary Science, Osaka Metropolitan University,

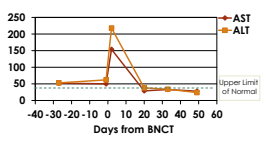


化学療法不応の多発肝転移症例

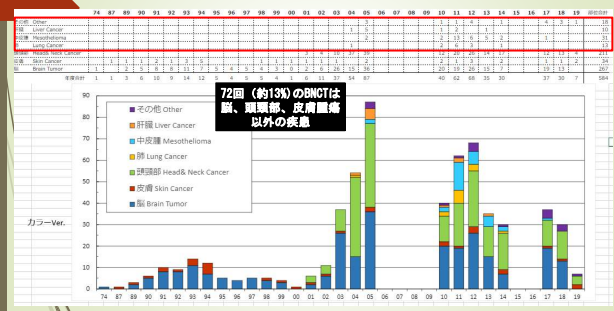
BNCT前後のCT画像



肝逸脱酵素 (AST, ALT) の遷移



京都大学複合原子力科学研究所・研究炉 (KUR) の症例 (癌種、症例数一覧)

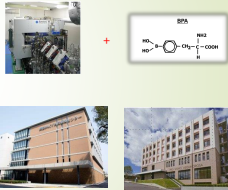


BNCTは医療機関にパトロンタッチ

原子炉



加速器



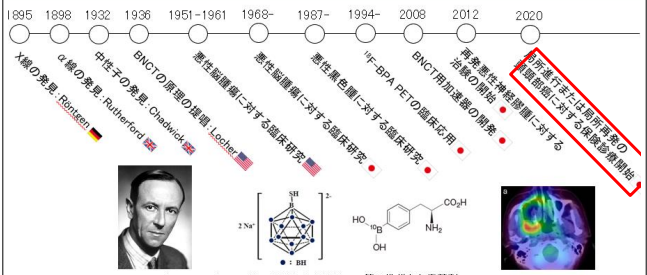
大学発研究の社会実装



関西BNCT共同利用センター

南東北BNCT研究センター

BNCTの歴史



Basic research for the application of BNCT in the veterinary field

Minoru Suzuki¹ Yusuke Wada^{1,2}, Takushi Takata¹

¹ Particle Radiation Oncology Research Center

Institute for Integrated Radiation and Nuclear Science, Kyoto University

² Veterinary Medical Center, School of Veterinary Science, Osaka Metropolitan University

Today's topics

1. Introduction

- Concept of "One Health" in BNCT research
- Clinical veterinary BNCT using a reactor and an accelerator.

2. Basic researches for the application of BNCT in the veterinary field

Background

Veterinary Medical Center (VMC)
at Osaka Metropolitan University
(OMU)



15 minutes
by car

Institute for Integrated Radiation and
Nuclear Science, Kyoto University
(KURUNS)



C-BENS
NeuCure

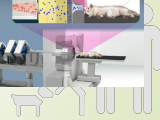
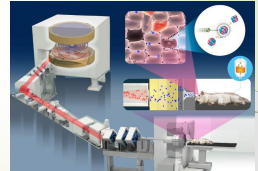
Collaborative research agreement has been signed.

Background

If a branch BNCT clinic (OMU) is settled at KURUNS, BNCT for
companion animals must be performed under the law (Veterinary
Practice Act).



C-BENS
NeuCure



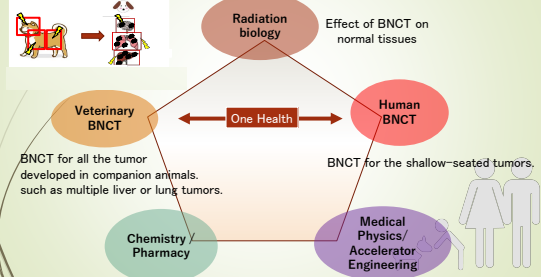
What is One Health ?

One Health is a **collaborative, multisectional, and transdisciplinary approach** — working at the local, regional, national, and global levels — with the **goal of achieving optimal health outcomes** recognizing the **interconnection between people, animals, plants, and their shared environment**.

Due to the commonality of human and animal diseases, **collaboration between medicine and veterinary medicine will improve the health of both.**

<https://www.cdc.gov/onehealth/basics/index.html>
One Health Basics | One Health | CDC

Collaborative, multisectional, and transdisciplinary approach in BNCT



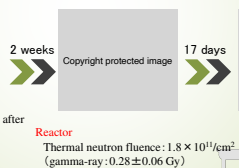
VET-BNCT-1

Available online at www.sciencedirect.com
Applied Radiation and Isotopes
BNCT of 3 cases of spontaneous head and neck cancer in feline patients
2004

SCC (Cats) (n = 3)

10B concentration ratio
Tumor/Blood
Case 1: 2.7
Case 2: 4.3
Case 3: 2.3, 2.6

*Measurement at 3 hours after the administration of BPA (300 mg/kg IV)



Response: 3 SD
Toxicity: none
Survival: 5 mo, 2.5 mo, 9.5 mo

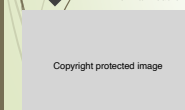
Rao M, et al. Appl Radiat Isot 2004;61:947-952

VET-BNCT-2

Applied Radiation and Isotopes
Comparison of BNCT and GdBNCT efficacy in treatment of canine cancer
2009

• Oral malignant melanoma (n = 33)
• Osteosarcoma in extremities (n = 9)

BPA 300 mg/kg IV or ^{157}Gd intratumorally
Reactor
Thermal neutron fluence: $2.97 \times 10^{17}/\text{cm}^2$



Mitri VN, et al. Appl Radiat Isot 2009;67:S299-S301

VET-BNCT-3

biology
Clinical Veterinary Boron Neutron Capture Therapy (BNCT) Studies in Dogs with Head and Neck Cancer: Bridging the Gap between Translational and Clinical Studies
2020

• Oral malignant melanoma (n = 2)
• Intranasal tumor (n = 3)

BPA : 350 mg/kg IV
Reactor
Dose: 30-52 Gy-Eq/ 2 Fr, q3-5 weeks

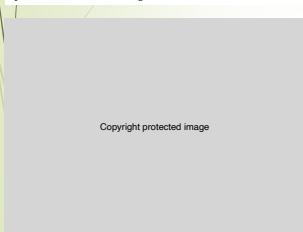


Response: 5 PR
Toxicity: mild-moderate mucositis

Schwint AE, et al. Biology. 2020;9:327.

VET-BNCT-4

biology
In Vivo Accelerator-Based Boron Neutron Capture Therapy for Spontaneous Tumors in Large Animals: Case Series
2022



BSH 100 mg/kg IV
Accelerator
Thermal neutron fluence
1.21-2.60 $\times 10^{19}/\text{cm}^2$
Tumor: 39.5-51.0 Gy-eq
Skin: 13.3-19.3 Gy-eq

No.	転帰
1	SD
2	PR
3	SD
4	SD
5	SD
6	PR
7	PR
8	SD
9	PR ?
10	Dye at a few hours after BNCT

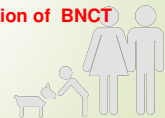
Kanygin V, et al. Biology. 2020;11:138.

Today's topics

1. Introduction

- Concept of "One Health" in BNCT research
- Clinical veterinary BNCT using a reactor and an accelerator.

2. Basic researches for the application of BNCT in the veterinary field



Question and answer session

Q: What are the common boron chemicals used overseas?

A: BPA is mainly used. Another boron scrubber called BSH is also used.

Q: How many pets are required?

A: We don't have an absolute number. The University's Veterinary Clinical Center is promoting the same, rather precise, radioactive treatment as for people.

Q: How can phosphorus 32 be produced?

A: Probably because the whole body was irradiated this time, so there is phosphorus in the feces in the abdomen, which is then radiolabeled.

Q: The whole body was irradiated this time, so such results were obtained. If the irradiation were limited to the head and neck, would the amount of phosphorus-32 emitted be less?

A: That is correct.

2.25 T. Suzuki (Nagaoka Univ. Tech.)

Dissolution of Thorium Oxide and Separation of Radium

酸化トリウムの溶解とラジウム分離

Dissolution of Thorium Oxide and Separation of Radium

鈴木達也、尹鳳、麻卓然
長岡技術科学大学

福谷 哲、外山真理、田端千紘、山村朝雄
京都大学複合科学研究所

1

現在検討している内容

Ac-225: $^{228}\text{Ra}(n,\gamma) \xrightarrow{5.75\text{y}} ^{229}\text{Ra} \xrightarrow{4.0\text{min.}} ^{229}\text{Ac} \xrightarrow{62.7\text{min.}} ^{229}\text{Th} \xrightarrow{7.34 \times 10^4\text{y}} ^{225}\text{Ra} \xrightarrow{14.9\text{d}} ^{225}\text{Ac} \xrightarrow{10.0\text{d}}$

②照射 ①抽出 ③分離 ④ジェネレータ

Th-decay series
 $^{232}\text{Th} \rightarrow ^{228}\text{Ra} \rightarrow ^{228}\text{Ac} \rightarrow ^{228}\text{Th} \rightarrow ^{224}\text{Ra} \rightarrow ^{220}\text{Rn} \rightarrow ^{216}\text{Po} \rightarrow ^{212}\text{Pb}$

希土類残渣等に含まれる
Th系列のRa-228を分離し、中性子を照射し、Ac-225を生成するジェネレータとする。

2

研究計画

Th化合物溶解・Ra-228抽出

- ・リーティング法による抽出
- ・化学転換法による溶解
- ・ピロリドン樹脂等吸着剤を用いた分離
- ・沈殿法等による分離

中性子照射用ターゲット作製

- ・中性子断面積の小さい母体を持った化学的に安定
- ・且つ照射後分離の容易な元素で構成されるターゲットの開発

中性子照射・照射後分離試験

- ・Ra-228の照射挙動の確認
- ・照射したターゲットからのTh-229の抽出分離
- ・Thを吸着させ、Acのみを分離する吸着剤(ジェネレータ)の開発

令和4年度～6年度までに実施予定
 令和4年度～6年度までに予算確保および準備ができれば実施したい。

3

化学転換による溶解法

Halides: $(\text{CCl}_3)_2$, CBr_4 , AlCl_3 , etc.

Dissolve in 30ml of conc. HCl or conc. HNO₃

4

溶解試験 CeO₂ を用いた予備実験

化学変換に適当なハロゲン化合物および条件を探る。 CCl_4 は比較のため実施。

塩酸で溶かした場合と硝酸で溶かした場合は塩酸の方が溶解率が高い傾向がある。

温度は溶解時間との相関が認められる。

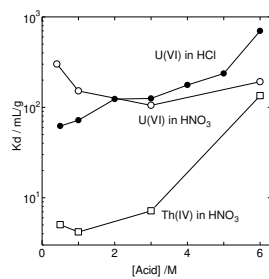
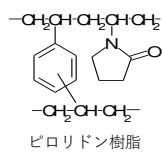
5

溶解試験 ThO₂ を用いた予備実験

実験条件:
 温度 300 °C
 加熱時間 4h
 塩酸で溶かした場合と硝酸で溶かした場合は塩酸の方が溶解率が高い傾向がある。
 CCl_3CCl_3 や CBr_4 が有効

6

ピロリドン樹脂を用いた核種吸着特性



20%架橋度のピロリドン樹脂を用いた吸着挙動。

Question and answer session

Q: ThO₂ is applied with hydrofluoric acid and nitric hydrofluoric acid, and radium ions are separated by ion exchange. Do you want to develop a new method?

A: Actually, we would like to separate them in one shot by precipitation method.

Q: If we use an aluminum compound as a source of halogen, won't aluminum do something bad?

A: Aluminum is not adsorbed, so separation is easy.

Q: Regarding thorium adsorption, why is there such a difference between hydrochloric acid and nitric acid?

A: It is the nature of actinides that nitric acid complexes well with tetravalent actinides, but hydrochloric acid does not.

Q: When adsorbing on pyrrolidone, what form does the actinide take?

A: This is the O of pyrrolidone.

Q: Is it the O in pyrrolidone and its interaction with nitric acid?

A: In the case of nitric acid, the nitric acid is complexed with thorium, and the whole thing becomes neutralized.

Q: Neutron irradiation of thorium 228 in a very long chain starting with thorium 232 will give thorium 229 in the (n, γ) reaction. What is the yield of thorium-229?

A: I think this is quite low.

Q: I am looking for data on the cross section of radium-228, but I can't find it.

A: I believe Nuclide Karte has a cross section for radium-228. It is not entirely absent. There was only one point.

Chapter 3 Y. Haga (ASRC, JAEA)

Concluding Remarks

Concluding remarks
on

Users meeting on Condensed-matter Chemistry
in Actinides and their Applications /
Production of medical RIs by Reactor Irradiation

Yoshinori Haga (JAEA)

- 基礎研究：アクチノイド、ランタノイド、超アクチノイド
- RI製造と応用
- 環境・安全・デブリ

KUR シャットダウン

ホットラボ拡充

福井研究炉

教育・人材育成

- 基礎研究：アクチノイド、ランタノイド、超アクチノイド
異分野（？）との交流・新たな視点

- RI製造と応用
大阪大学の取り組み
アメリカの状況（国立研究所、大学、民間）

- 環境・安全・デブリ
計算科学の活用、実用化

研究コミュニティの形成へー研究資金獲得
京都大学・文科省
科研費（学術変革領域等）
多分野をつなぐ共通概念を柱に

ハイブリッド会議の有効活用！

Actinides 2023
HOME SCHEDULE ABSTRACT SUBMISSION LOCATION LOGGING ORGANIZERS
POSTER TRAVEL CONTACT
Actinides 2023
COLORADOSCHOOL OF MINES
Golden Colorado
June 5-8, 2023
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
Rf Db Sg Bh Hs Mt Ds Rg Cn Nh Fl Mc Lv Ts Og
Actinides 2023

Q: I would like to ask a question on my part. I would like to talk about the previous slide in terms of a common concept to connect communities and other fields as a pillar. I showed you the concept at the time of the foundation S by Prof. Noriaki Sato at Tohoku University, centering on the alpha radiator laboratory, in my first talk yesterday, where chemistry and physics are in that intermediate region between 4f localization and d itinerancy in terms of the speed of valence fluctuation of the 5f electron, both in physics and chemistry, It was a common understanding that it was very interesting, and it all came from there. There was J-Physics in the field of condensed matter physics.

A: It is over, but its successor will start this year. It will probably be a little different.

Q: J-Physics must have some kind of interdisciplinarity, but what is the central concept that connects the two? If there are two J-Physics programs, what is the central concept of each?

A: First of all, J-Physics is f-orbital. f-orbital is the orbital nuclear momentum ($SP1/2$), which is called freedom, and the total angular momentum J is the J in J-Physics, and we are trying to investigate how the degree of freedom is reflected in physical properties, both in discussions and experiments. The keywords are the orbitals and charge distribution, and there was a trend to expand the charge distribution by multipoles and organize it. In the upcoming J-Physics project, the idea of extending this idea to include not only one atom but also other atoms in the charge distribution by using extended multipoles was proposed and established theoretically. It is like scaling it up to make it with real materials this time, and is an area where material exploration is very much in the spotlight.

Thank you very much.

We have been allowed to proceed in the form of the fourth time so far. It is still necessary to think about how we are thinking about something that connects all of you, like an adhesive. First of all, we are all connected through the use of this facility at Kyoto University, so even if there is talk of a shutdown in the future, we need to think in such a way that we can be connected within that context, and since we are now considering new facilities such as a hot laboratory,

we need to consider such things to some extent. We would be very happy if we could create a place where everyone can interact with each other while considering such a possibility to some extent. I hope that you will actively participate in the conference.

Thank you very much for your very useful reports and discussions during the two long days. Thank you very much. Thank you very much. I would like to find some kind of group, some kind of concept that can be connected, including the things you just mentioned. Also, I hope we can create a ripple effect.

Chapter 4 Summary of Discussion

Active discussions were held on the fundamentals and applications of actinide property chemistry. The interests and issues raised by the speakers can be found in their respective presentation materials. The community of basic actinide science (physics, chemistry, medical science, materials science, etc.) is small. In contrast, this field becomes more important as many new subjects appear, presented in this workshop. Considering the current situation, it is quite important to promote the collaborations between actinide researchers of different fields over the world.

The importance of the emerging young researcher who can act as an intermediary between basic research and nuclear engineering was strongly pointed out. For the purpose, the organization of a new international collaboration system for wide actinide research by the young researchers was mentioned of.

Concluding remark was also given from the theoretical side. Key points in this meeting are (1) 5f electrons in actinides and (2) basic character of 5f electrons. The latter include actinide contraction, relativistic effect, and occupation number and valence (common in physics and chemistry) electron configuration.

Chapter 5 List of Participants

The following people participated in the meeting. Thank you very much.

Participants	affiliations
Kenji Shirasaki	IMR, Tohoku University
Dexin Li	Institute for Materials Research Actinide Materials Science, Tohoku University
Hiroki Shishido	Tohoku University
Kohshin Washiyama	Advanced Clinical Research Center, Fukushima Global Medical Science Center, Fukushima Medical University
Masahiko Nakase	Tokyo Institute of Technology
Tatsuya Suzuki	Nagaoka University of Technology
Koki Yamamoto	Kyoto University
Minoru Suzuki	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Tomoo Yamamura	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Masaaki Sugiyama	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Tsuyoshi Misawa	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Yoshinori Sakurai	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Koichi Takamiya	KURNS, Kyoto Univ.
Mari Toyama	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Nobuhiro Sato	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Natsuko Kondo	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Toshimasa Yoshiie	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Hisao Yoshinaga	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Miki Tanihira	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Tsubasa Watanabe	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Yuji Kawabata	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Yasuko Marui	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Toshiharu Takahashi	Institute for Integrated Radiation and Nuclear Science, Kyoto University
Yuji Nakamoto	Kyoto University
Yoichi Shimizu	Radiology and Nuclear Medicine Service, Hospital, Kyoto University
Takumi Saito	Kyoto University
Kenji Ishida	Kyoto University
Takashi Yoshimura	Radioisotope Research Center, Institute for Radiation Sciences, Osaka University
Yoshitaka Kasamatsu	Graduate School of Science, Osaka University
Takamitsu Fukuda	Graduate School of Science Department of Chemistry, Osaka University
Minoru Abe	Hiroshima University
Takafumi Kitazawa	Department of Chemistry, Faculty of Science, Toho University
Masanobu Nogami	Kindai University
Hidetaka Nakai	Kindai University
Yoshinori Haga	Advanced Science Research Center, Japan Atomic Energy Agency
Tohru Kobayashi	Actinide chemistry group, Materials Sciences research center, Japan Atomic Energy Agency
Kenji Yoshii	Japan Atomic Energy Agency
Sho Tokunaga	Japan Atomic Energy Agency

Participants	affiliations
Kazufumi Tsujimoto	Japan Atomic Energy Agency
Tsuyoshi Yaita	Japan Atomic Energy Agency
Yuma Sekiguchi	Central Research Institute of Electric Power Industry
Takahito Watanabe	Hitachi, Ltd.
Mizuho Maeda	Hitachi, Ltd.
Takahiro Sasaki	Hitachi, Ltd.
Taisuke Tsukamoto	
Takashi Shimada	Mitsubishi Heavy Industries, Ltd.
Hiroyuki Kimura	Kyoto Pharmaceutical University
Rob Hall	MURR, Missouri University
Fukasawa Tetsuo	NFD
Toro Gonzalez	Oak Ridge National Laboratory
Laetitia H. Delmau	Oak Ridge National Laboratory
Julie G. Ezold	Oak Ridge National Laboratory
Greg Piefer	SHINE Technologies, Inc.
Hiroshi Yamagami	Kyoto Sangyo University
Ayumi Ishii	Teikyo University of Science

Chapter 6 Photos of the workshop

Photos of the lectures are shown in the order of the program.



Fig. 6.1: Tomoo Yamamura, KURNS, Kyoto Univ.

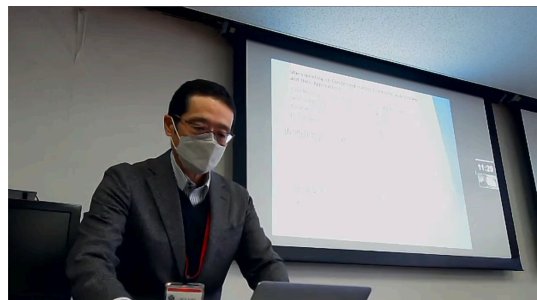


Fig. 6.2: Hiroshi Yamagami, Kyoto Sangyo University

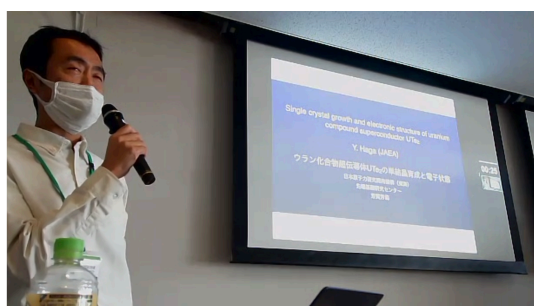


Fig. 6.3: Yoshinori Haga, Advanced Science Research Center, Japan Atomic Energy Agency

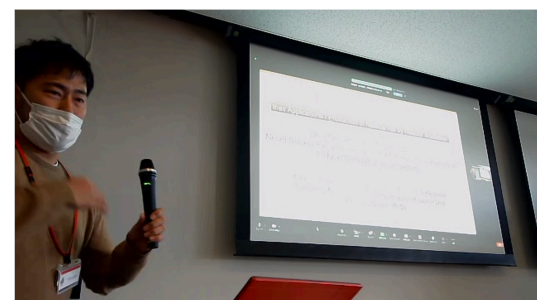


Fig. 6.4: Masahiko Nakase, Tokyo Institute of Technology



Fig. 6.5: Ayumi Ishii, Teikyo University of Science



Fig. 6.6: Masanobu Nogami, Kindai University

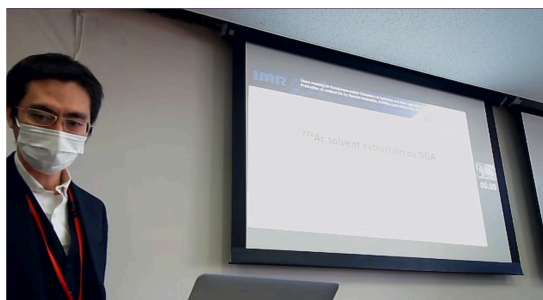


Fig. 6.7: Kenji Shirasaki, IMR, Tohoku University



Fig. 6.8: Tohru Kobayashi, Actinide chemistry group, Materials Sciences research center, Japan Atomic Energy Agency



Fig. 6.9: Yoshitaka Kasamatsu, Graduate School of Science, Osaka University



Fig. 6.10: Takashi Yoshimura, Radioisotope Research Center, Institute for Radiation Sciences, Osaka University



Fig. 6.11: Yoshinori Sakurai, KURNS, Kyoto Univ.

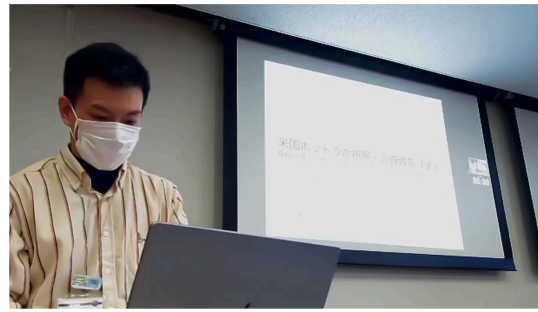


Fig. 6.12: Hisao Yoshinaga, KURNS, Kyoto Univ.

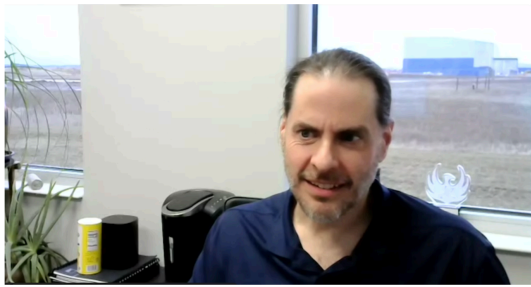


Fig. 6.13: Greg Piefer, SHINE Technologies, Inc.



Fig. 6.14: Laetitia H. Delmau, Oak Ridge National Laboratory

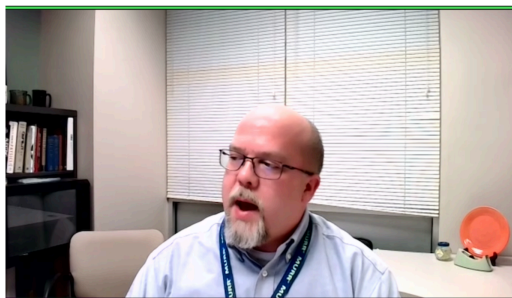


Fig. 6.15: Rob Hall, MURR, Missouri University

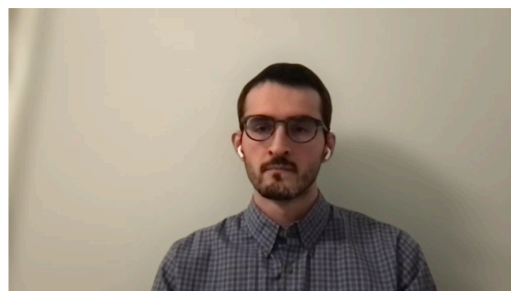


Fig. 6.16: Toro Gonzalez, Oak Ridge National Laboratory



Fig. 6.17: Julie G. Ezold, Oak Ridge National Laboratory



Fig. 6.18: Kenji Ishida, Kyoto University



Fig. 6.19: Hiroki Shishido, Tohoku University



Fig. 6.20: Minori Abe, Hiroshima University



Fig. 6.21: Hiroyuki Kimura, Kyoto Pharmaceutical University



Fig. 6.22: Minoru Suzuki, KURNS, Kyoto Univ.



Fig. 6.23: Tatsuya Suzuki, Nagaoka University of Technology