2020.08.11 （第三届“非传统稳定同位素地球化学”暑期学校）

非传统同位素的核场位移（核体积）效应

刘 耘

成都理工大学

中国科学院地球化学研究所

稳定同位素分馏理论分类

- 平衡分馏理论
- 稳态（动态平衡）分馏理论
- 动力学分馏理论
- 非平衡分馏理论

稳定同位素地球化学的理论基石


Harold C. Urey


Jacob Bigeleisen

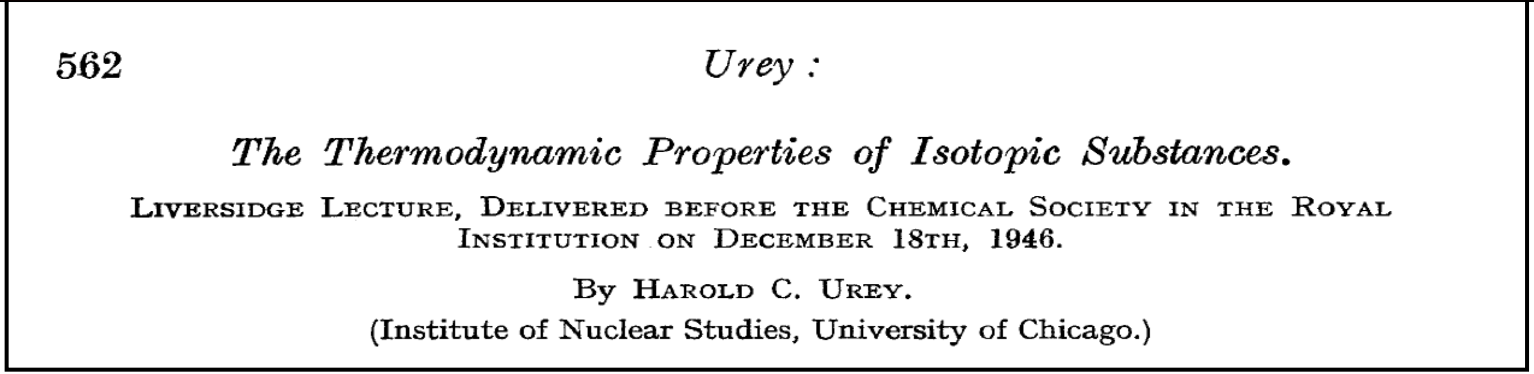

Maria G. Mayer

Urey model or Bigeleisen-Mayer equation

思想：能量决定稳定同位素平衡分馏大小

同位素分馏系数 ⟷ 配分函数 Q

Bigeleisen-Mayer公式



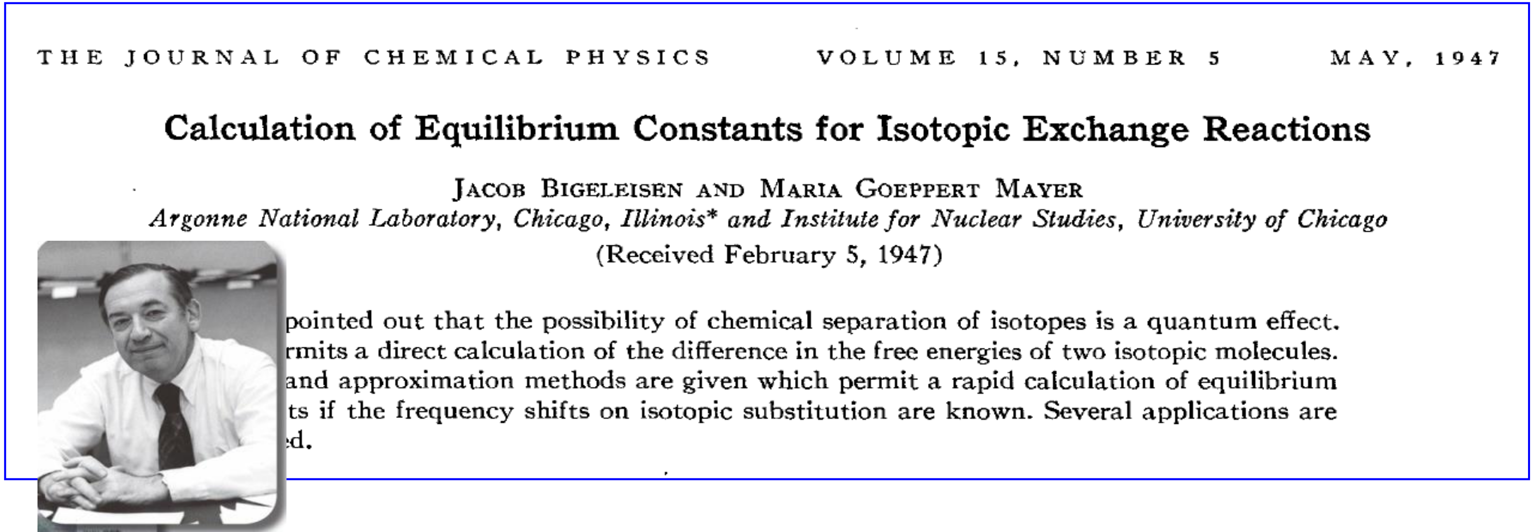
562 *Urey :*

The Thermodynamic Properties of Isotopic Substances.

LIVERSIDGE LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY IN THE ROYAL INSTITUTION ON DECEMBER 18TH, 1946.

By HAROLD C. UREY.

(Institute of Nuclear Studies, University of Chicago.)



THE JOURNAL OF CHEMICAL PHYSICS VOLUME 15, NUMBER 5 MAY, 1947

Calculation of Equilibrium Constants for Isotopic Exchange Reactions

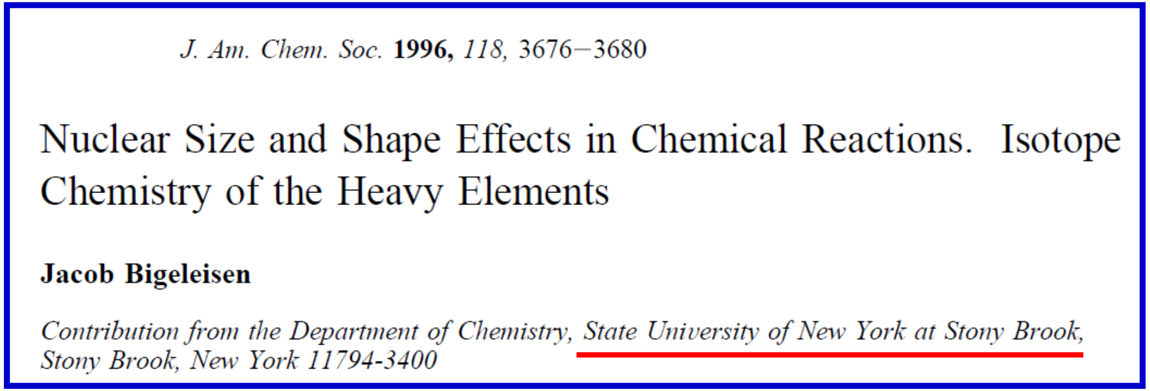
JACOB BIGELEISEN AND MARIA GOEPPERT MAYER

Argonne National Laboratory, Chicago, Illinois and Institute for Nuclear Studies, University of Chicago*

(Received February 5, 1947)

pointed out that the possibility of chemical separation of isotopes is a quantum effect. rmits a direct calculation of the difference in the free energies of two isotopic molecules. and approximation methods are given which permit a rapid calculation of equilibrium ts if the frequency shifts on isotopic substitution are known. Several applications are d.

同位素平衡分馏理论



J. Am. Chem. Soc. **1996,** *118,* 3676–3680

Nuclear Size and Shape Effects in Chemical Reactions. Isotope Chemistry of the Heavy Elements

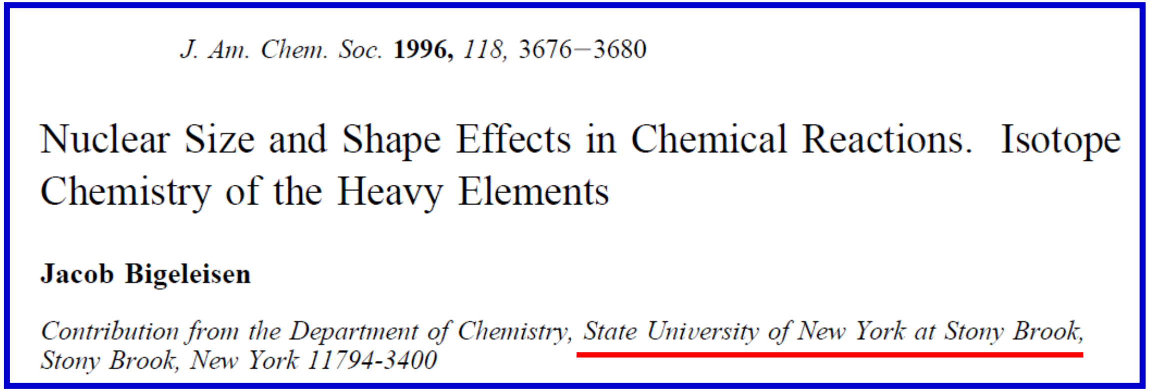
Jacob Bigeleisen

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400

Bigeleisen

$$\ln\alpha=\ln\alpha_0+\ln K_{anh}+\ln K_{BOELE}+\ln K_{hf}+\ln K_{fs}$$

同位素平衡分馏理论



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非简谐校正

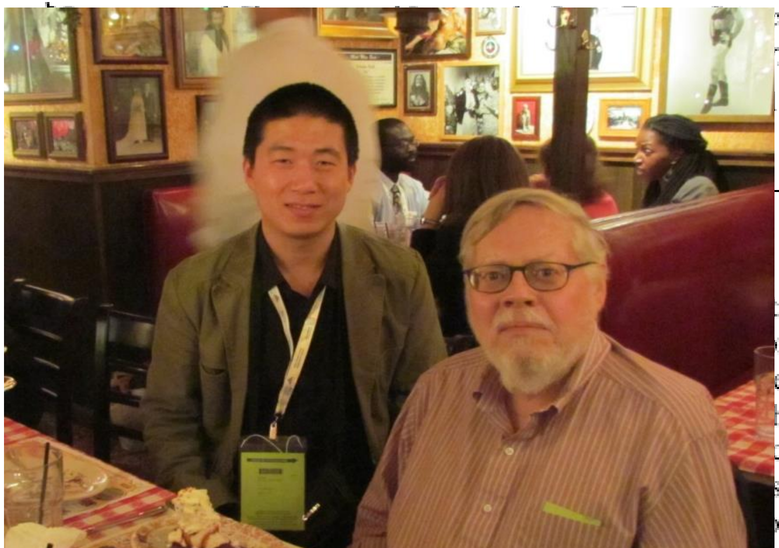
Acta
ELSEVIER
Geochimica et Cosmochimica Acta 74 (2010) 6965–6983
www.elsevier.com/locate/gca

On the proper use of the Bigeleisen–Mayer equation and corrections to it in the calculation of isotopic fractionation equilibrium constants

Qi Liu [a], John A. Tossell [b,c], Yun Liu [a,*]

[a] State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China
ce and Technology, George Washington University, Washington, DC 20052, USA
ry, University of Maryland, College Park, MD 20742, USA

form 7 September 2010; available online 17 September 2010



ical corner-stone of stable isotope geochemistry for decades. It is nec-
f the approximations and the Teller–Redlich product rule employed
e the publication of the Bigeleisen–Mayer equation in 1947, many
hey either directly used experimentally observed fundamental frequen-
city contributions, or used harmonic frequencies from quantum chem-
s to fit the experimentally observed fundamentals. Such errors have
on of equilibrium isotopic fractionation. Moreover, many researchers

前人的非谐校正工作

Richet et al. (1977)

- Anharmonicity of ZPE
- Anharmonicity of Vibrational Excited States
- Vib-Rot Coupling of ZPE
- Vib-Rot Coupling of Vibrational Excited States
- Quantum Mechanical Rotation

我们（2010年）的非谐校正工作

Liu, Tossell, Liu (2010):

- Anharmonicity of ZPE (**AnZPE**)
- Anharmonicity of Vib Excited States (AnEXC)
- Vib-Rot Coupling of ZPE (**VrZPE**)
- Vib-Rot Coupling of Vibrational Excited States (**VrEXC**)
- Quantum Mechanical Rotation (**QmCorr**)
- Centrifugal Distortion (**CenDist**)
- Hindered Internal Rotation (**Torsion**)
- ……

我们（2018年）的非谐校正工作

ELSEVIER

Geochimica et Cosmochimica Acta 238 (2018) 123–149

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The theory of equilibrium isotope fractionations for gaseous molecules under super-cold conditions

Yining Zhang[a,b], Yun Liu[a,*]

[a] State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China

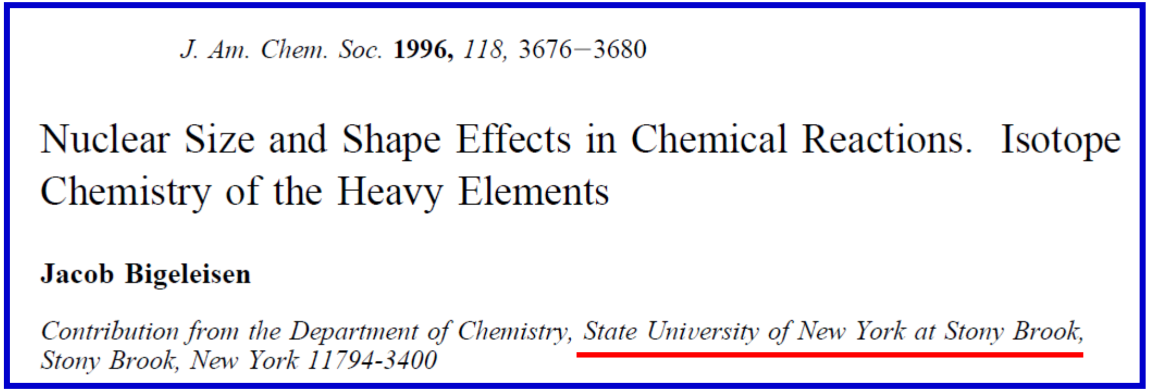
Received 28 February 2018; accepted in revised form 1 July 2018; Available online 09 July 2018

Abstract

It is necessary to build a proper theoretical method that can precisely describe isotope fractionation processes under super-cold (<200 K) conditions, because there have been many isotopic data obtained in our solar system that are related to such processes. However, current methods of isotope fractionation calculation, i.e., the Bigeleisen-Mayer equation and its higher-order energy corrections, may not be applicable to super-cold conditions. Here, we have checked important assumptions and higher-order corrections that can affect isotope fractionations of gas-phase molecules under super-cold conditions and developed a new theoretical method for calculating equilibrium isotope fractionation factors. Compared with previous works, we have added three new corrections into our calculation, i.e., nuclear-spin weights for quantum mechanical rotation, correction for Born-Oppenheimer approximation (BOA), and inversion splitting effect for non-planar molecules such as NH_3. We further examined gaseous molecules of geochemistry and cosmochemistry relevance, e.g., H_2, HF, HCl, H_2O, H_2S, HCHO, NH_3, CH_4 and their deuterated isotopologues. We found that the correction for BOA, which was rarely considered in previous studies, is important for those gaseous molecules under super-cold conditions. In case of D/H, $^{13}C/^{12}C$ and $^{18}O/^{16}O$ exchanges among organic molecules, BOA correction cannot be ignored even at ambient or higher temperature conditions. Most isotope fractionation trends at super-cold conditions reported here are quite different from their counterparts at ambient or higher temperature conditions. The method proposed here will extend our capability in interpreting equilibrium isotope fractionations to super-cold conditions in the solar system.

- **Nuclear-spin weights for quantum rotation**
- **B-O近似的修正**
- **Inversion splitting effect for non-planar molecules**

同位素平衡分馏理论



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Bigeleisen

$$\ln\alpha=\ln\alpha_0+\ln K_{anh}+\ln K_{BOELE}+\ln K_{hf}+\ln K_{fs}$$

波恩-奥本海默近似所忽略的
同位素分馏校正

The correction for BOA (Born-Oppenheimer Approximation)

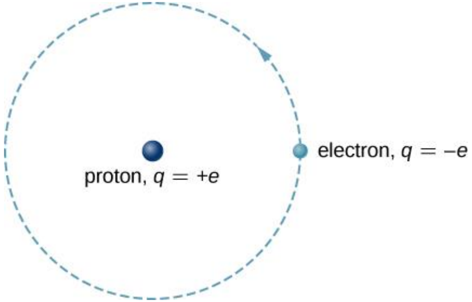
BOA: The kinetic motions of electrons and nuclei are independent.

Correction： Coupling between the electronic and nuclear wavefunction

The correction for the Born-Oppenheimer Approximation via DBOC (Diagonal Born-Oppenheimer Correction)

DBOC Firstly proposed by Born and Huang (1956).

A first-order perturbative energy correction for the BOA.



$$\left(-\frac{1}{2m_e}\nabla_e^2 - \frac{e}{4\pi\varepsilon_0\left|\mathbf{r}_e - \mathbf{R}_p\right|}\right)\Psi = E_2\Psi$$

BO

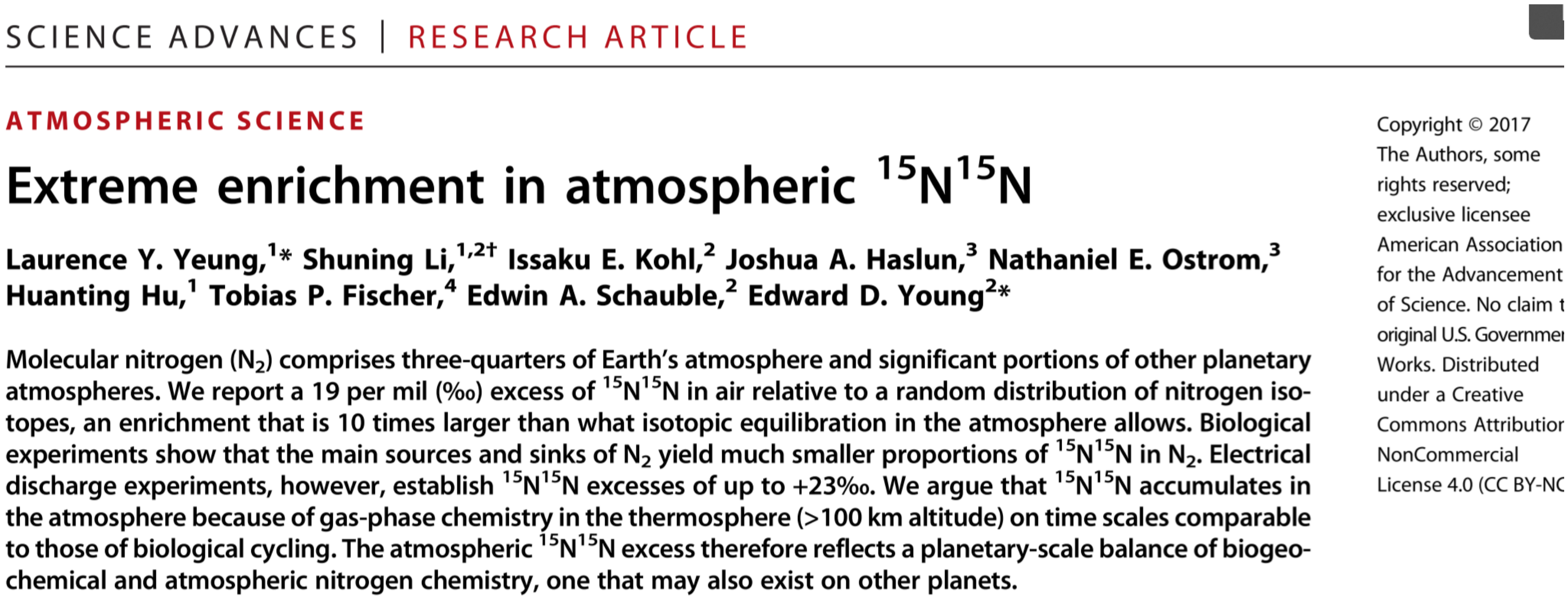
$$\left(-\frac{1}{2m_p}\nabla_p^2 - \frac{1}{2m_e}\nabla_e^2 - \frac{e}{4\pi\varepsilon_0\left|\mathbf{r}_e - \mathbf{R}_p\right|}\right)\Psi = E_1\Psi$$

Non-BO

E_1	E_2	E_1 - E_2	E_{DBOC} (Our result)
-13.59828667 eV	-13.60569253 eV	0.00740586 eV	0.00739960 eV

H: E_{DBOC} includes > 99.9% non-BO energy

Hyper-clumping of $^{15}N^{15}N$ in atomsphere



SCIENCE ADVANCES | RESEARCH ARTICLE

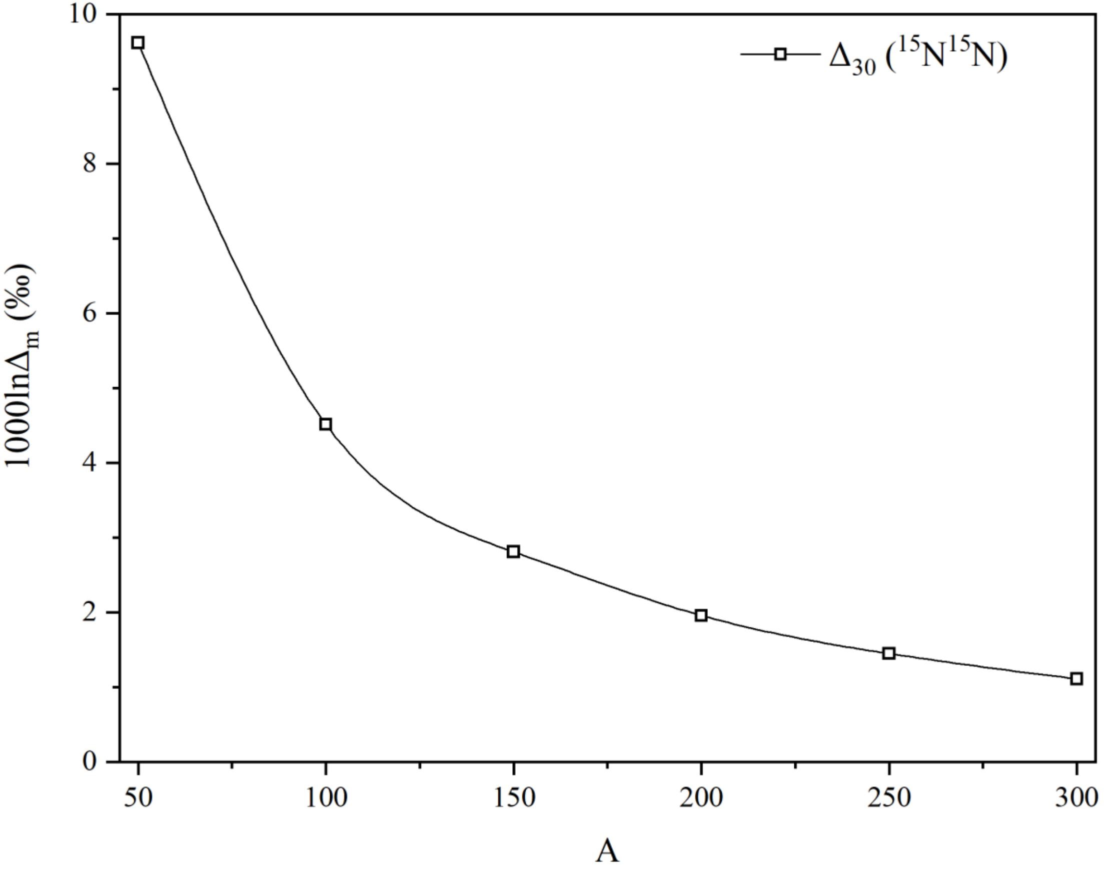
ATMOSPHERIC SCIENCE

Extreme enrichment in atmospheric $^{15}N^{15}N$

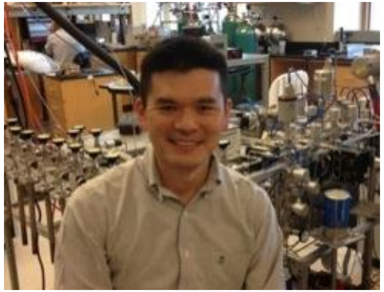
Laurence Y. Yeung,[1]* Shuning Li,[1,2]† Issaku E. Kohl,[2] Joshua A. Haslun,[3] Nathaniel E. Ostrom,[3] Huanting Hu,[1] Tobias P. Fischer,[4] Edwin A. Schauble,[2] Edward D. Young[2]*

Molecular nitrogen (N_2) comprises three-quarters of Earth's atmosphere and significant portions of other planetary atmospheres. We report a 19 per mil (‰) excess of $^{15}N^{15}N$ in air relative to a random distribution of nitrogen isotopes, an enrichment that is 10 times larger than what isotopic equilibration in the atmosphere allows. Biological experiments show that the main sources and sinks of N_2 yield much smaller proportions of $^{15}N^{15}N$ in N_2. Electrical discharge experiments, however, establish $^{15}N^{15}N$ excesses of up to +23‰. We argue that $^{15}N^{15}N$ accumulates in the atmosphere because of gas-phase chemistry in the thermosphere (>100 km altitude) on time scales comparable to those of biological cycling. The atmospheric $^{15}N^{15}N$ excess therefore reflects a planetary-scale balance of biogeochemical and atmospheric nitrogen chemistry, one that may also exist on other planets.

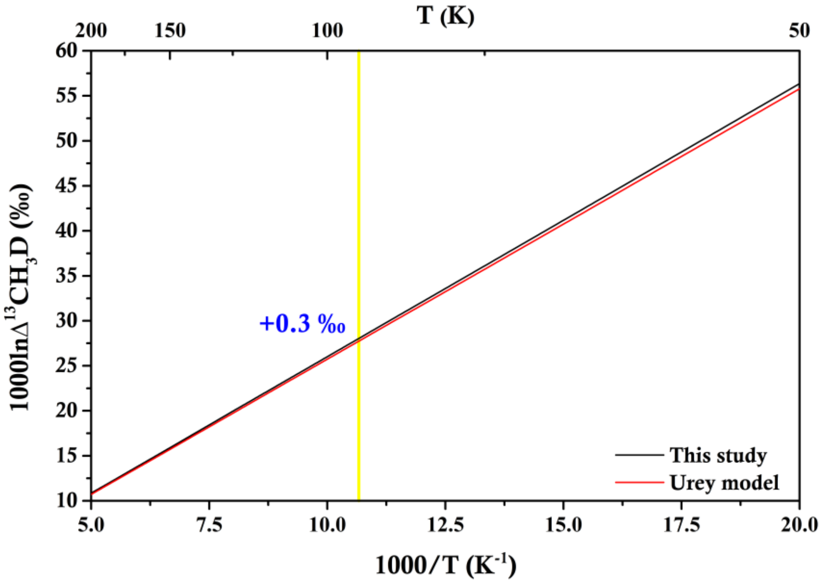
Equilibrium clumping of $^{15}N^{15}N$ in atomsphere

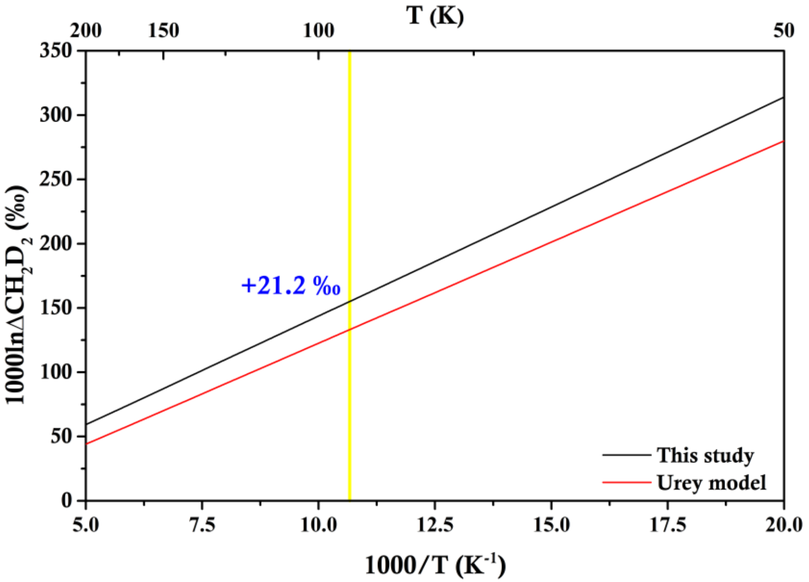


$^{13}CH_3D$ and $^{12}CH_2D_2$

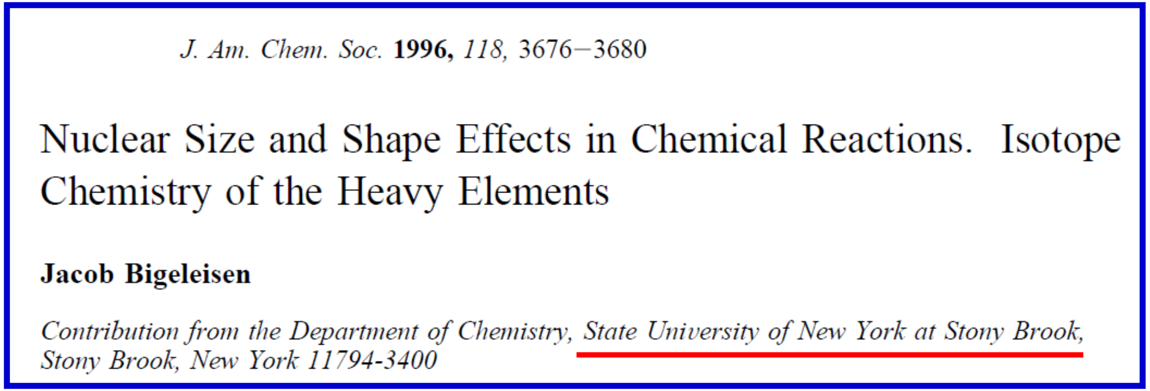


Shuhei Ono





同位素平衡分馏理论



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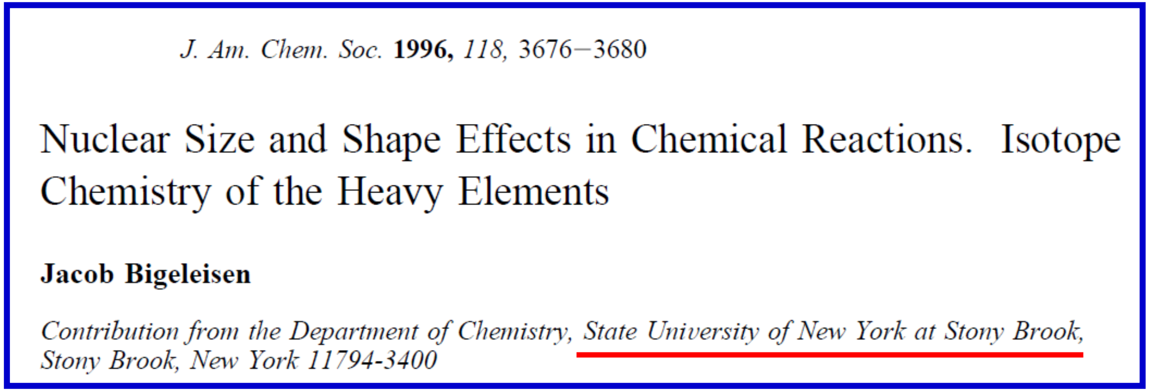
核自旋（核磁）同位素平衡分馏校正

同位素平衡分馏理论



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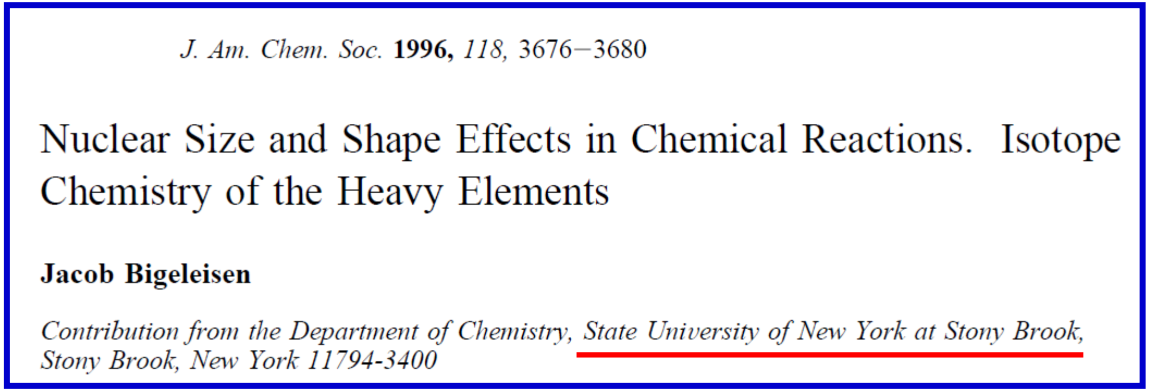
核场位移（核体积）同位素平衡分馏校正

同位素平衡分馏理论



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+ 压力效应

The theoretical treatment of Polyakov

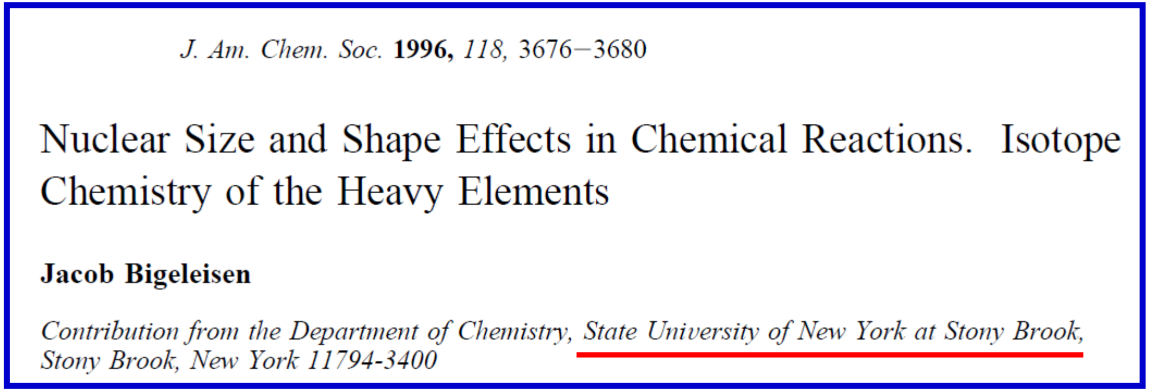
$$
\begin{aligned}
&G\left(T,P,m^{*}\right)-G\left(T,P,m\right)\\
&=F\left(T,V^{*},m^{*}\right)-F\left(T,V,m\right)+P\Delta V\\
&\approx F\left(T,V,m^{*}\right)+\left(\frac{\partial F\left(T,V,m^{*}\right)}{\partial V}\right)\Delta V-F\left(T,V,m\right)+P\Delta V\\
&=F\left(T,V,m^{*}\right)-F\left(T,V,m\right)
\end{aligned}
$$

First-order of Taylor expansion

The two ways to obtain Helmholtz free energy:

- Quasi-harmonic
- Intrinsic anharmonic

同位素平衡分馏理论



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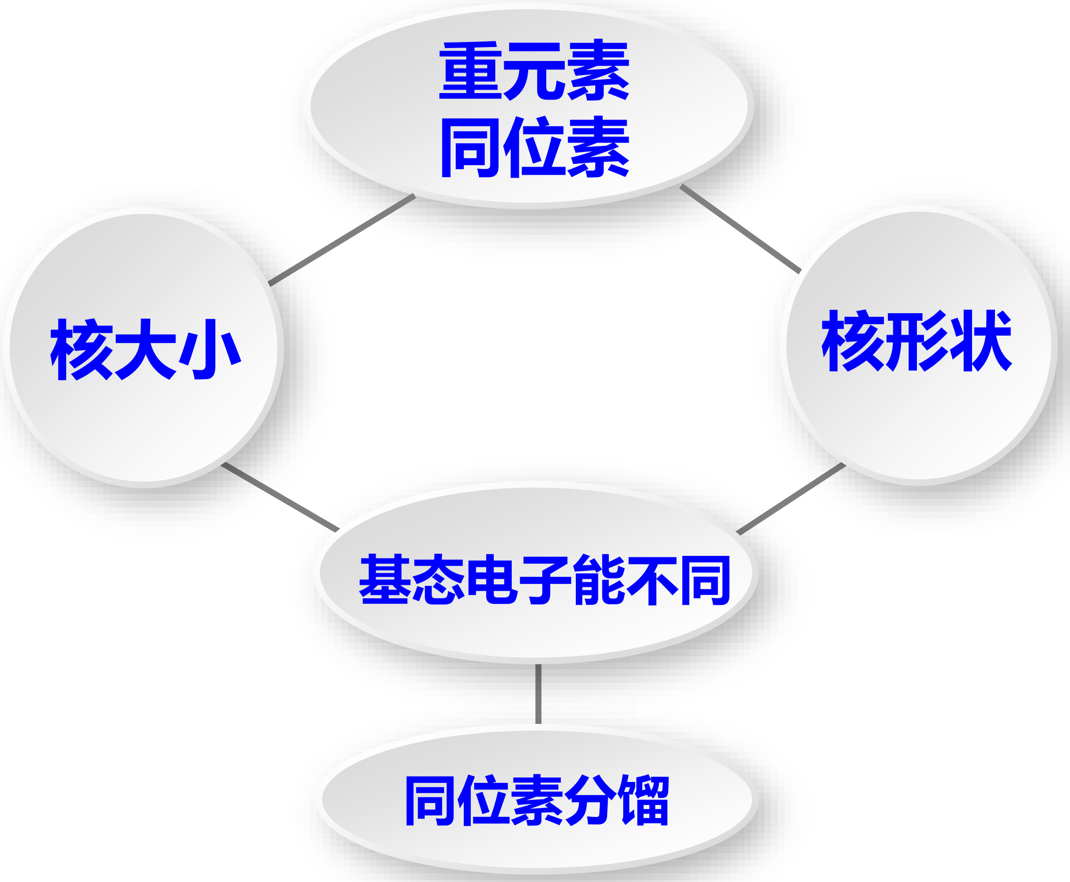
核场位移（核体积）同位素平衡分馏校正

非传统稳定同位素对同位素理论体系的最重要的贡献：

核场位移（核体积）效应

真正的创新是对理论体系的改变

-- 陈 丰


重元素
同位素

核大小

核形状

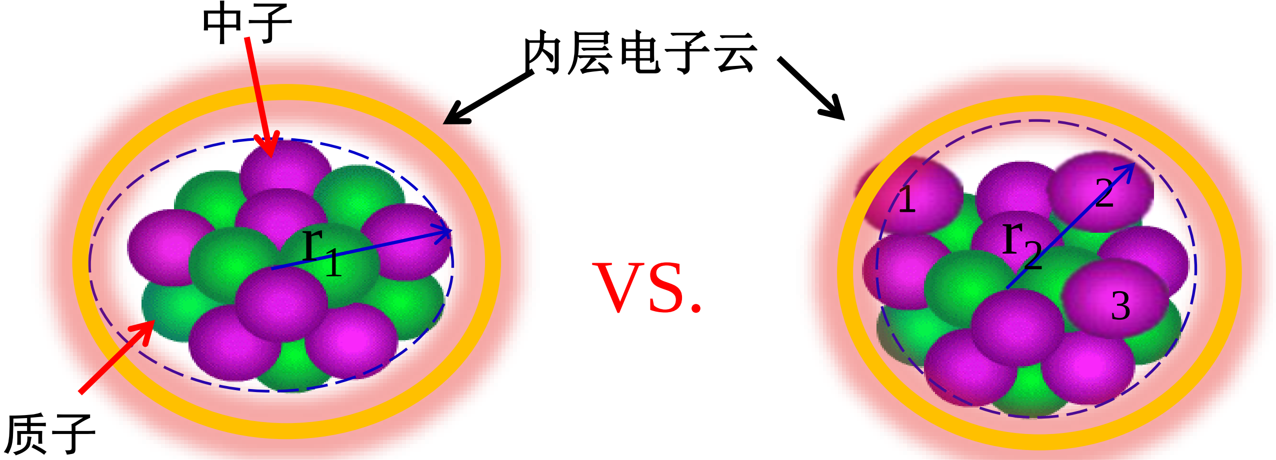
基态电子能不同

同位素分馏

NVE

Nuclear Volume Effect

核体积效应



核1（如^{235}U）

$\langle r_1 \rangle^{1/2}$=5.82 (fm)

核2（如^{238}U)

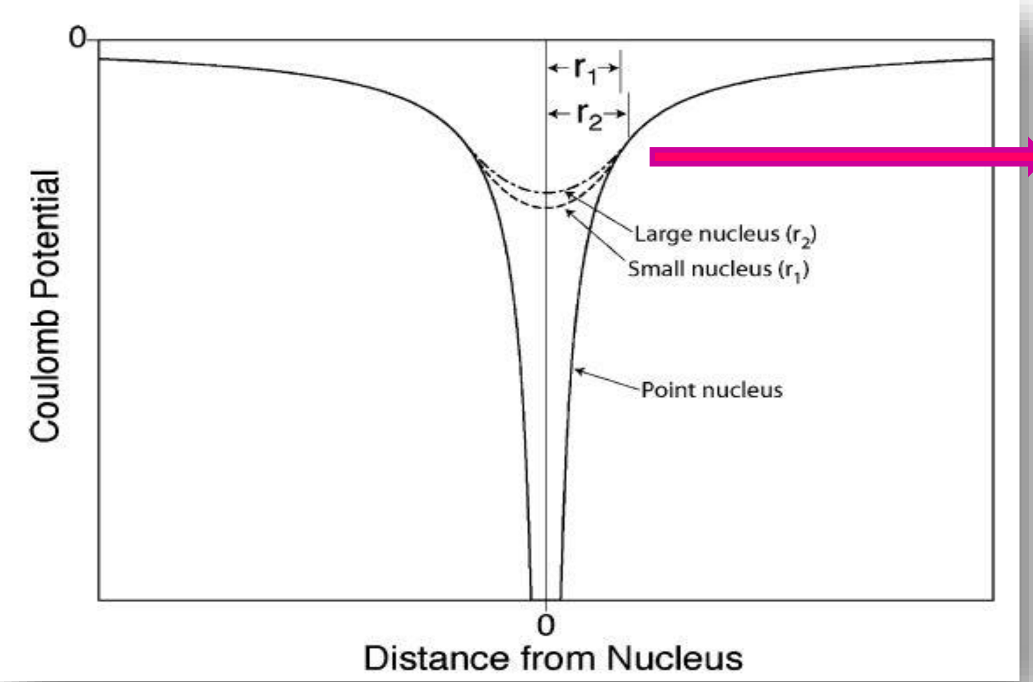
$\langle r_2 \rangle^{1/2}$=5.85 (fm)

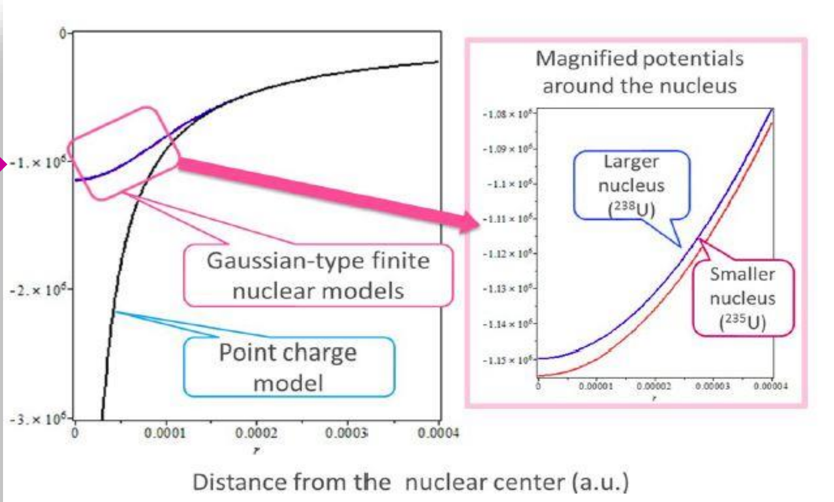
导致同位素的电子能不同：

$^{235}U^{+6}$ = -28052.2068（a.u.）

$^{238}U^{+6}$ = -28052.1095（a.u.）

核体积效应

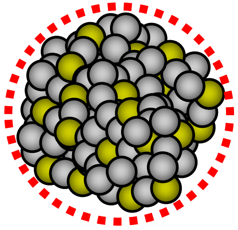




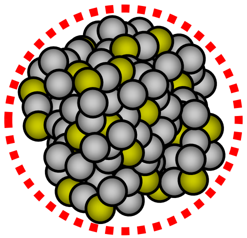
(Schauble, 2007）

重元素同位素的电子能不同。这种差异会引起同位素的分馏。

$^{235}\mathrm{U}$



$^{238}\mathrm{U}$



$R_{av} = 5.8337(41)$ fm

$R_{av} = 5.8571(33)$ fm

1 fm = 10^{-15} m

http://www-nds.iaea.org/radii/#ref

原子核电荷半径的差异

↓

库伦吸引势能的差别

$$^{238}\mathrm{U}^{6+} + {}^{235}\mathrm{U}^{4+} = {}^{238}\mathrm{U}^{4+} + {}^{235}\mathrm{U}^{6+}$$

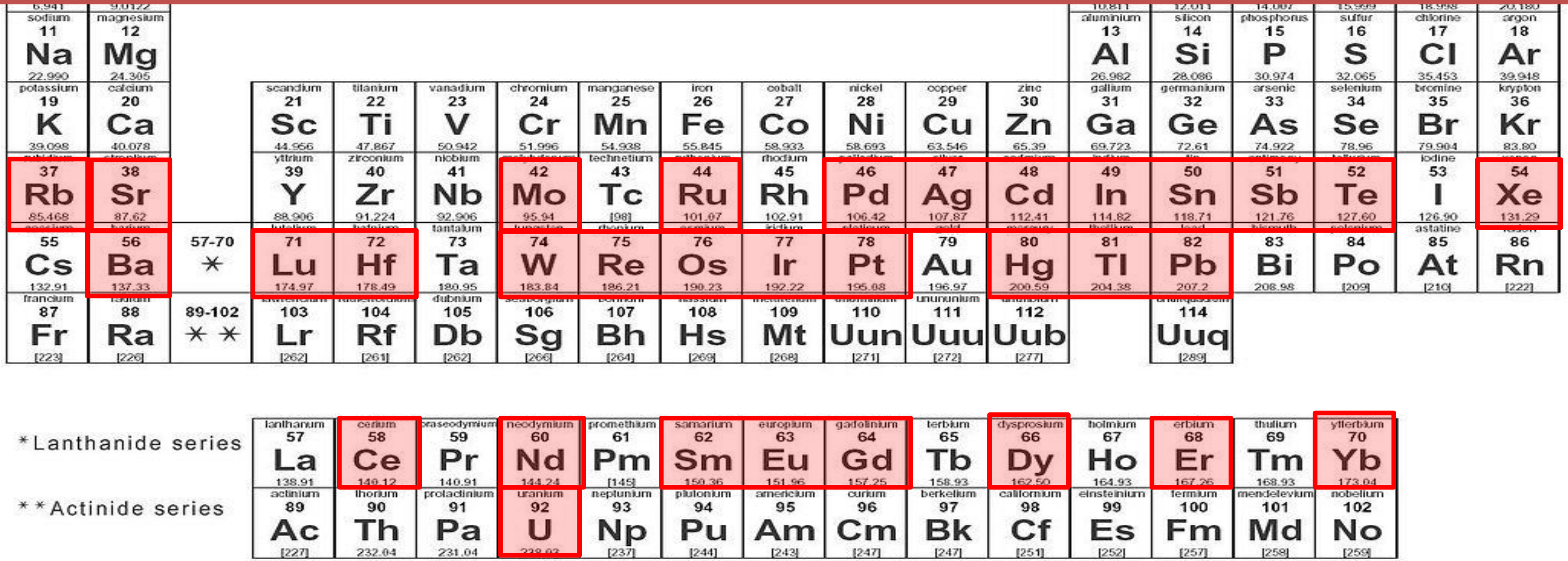
$$\Delta E = 4.030\times10^{-5}\ \mathrm{eV}$$

Bigeleisen (1996, JACS)

$$K_{fs} = 1.00108\ (433\ \mathrm{K})$$

核体积效应

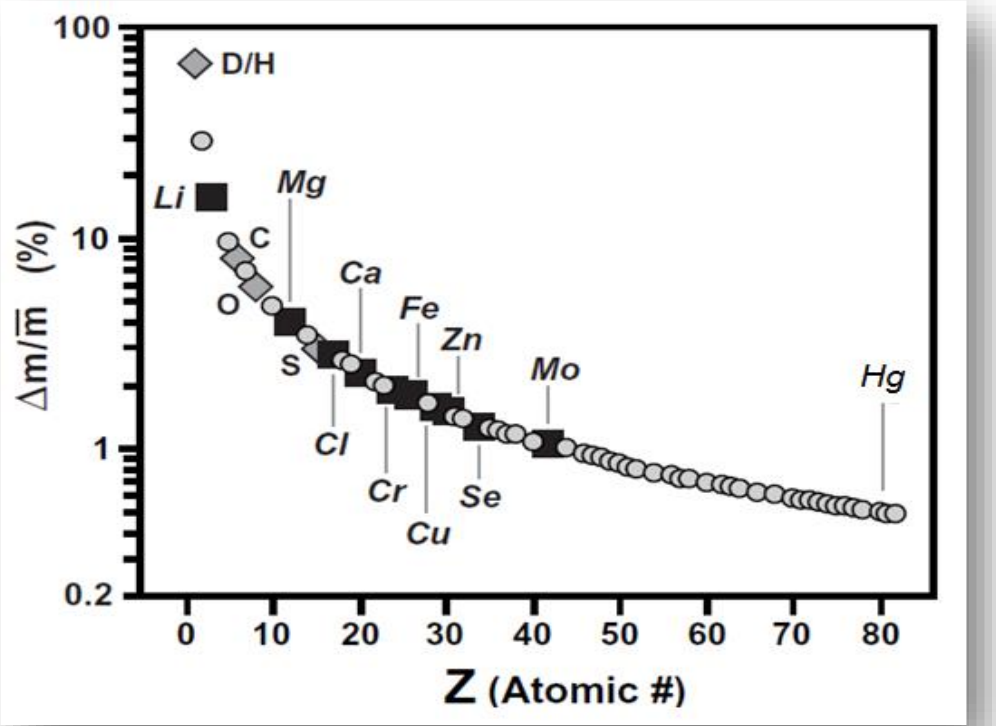
具较显著核体积效应的体系



6.941	9.0122												10.811	12.011	14.007	15.999	18.998	20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
37 **Rb** **85.468**	**38** **Sr** **87.62**		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	**42** **Mo** **95.94**	technetium 43 Tc [98]	**44** **Ru** **101.07**	rhodium 45 Rh 102.91	**46** **Pd** **106.42**	**47** **Ag** **107.87**	**48** **Cd** **112.41**	**49** **In** **114.82**	**50** **Sn** **118.71**	**51** **Sb** **121.76**	**52** **Te** **127.60**	iodine 53 I 126.90	**54** **Xe** **131.29**
55 Cs 132.91	**56** **Ba** **137.33**	57-70 *	**71** **Lu** **174.97**	**72** **Hf** **178.49**	tantalum 73 Ta 180.95	**74** **W** **183.84**	**75** **Re** **186.21**	**76** **Os** **190.23**	**77** **Ir** **192.22**	**78** **Pt** **195.08**	79 Au 196.97	**80** **Hg** **200.59**	**81** **Tl** **204.38**	**82** **Pb** **207.2**	83 Bi 208.98	84 Po [209]	astatine 85 At [210]	86 Rn [222]
francium 87 Fr [223]	88 Ra [226]	89-102 * *	103 Lr [262]	104 Rf [261]	dubnium 105 Db [262]	106 Sg [266]	107 Bh [264]	108 Hs [269]	109 Mt [268]	110 Uun [271]	ununnunium 111 Uuu [272]	112 Uub [277]		114 Uuq [289]				

*Lanthanide series	lanthanum 57 La 138.91	**cerium** **58** **Ce** **140.12**	praseodymium 59 Pr 140.91	**neodymium** **60** **Nd** **144.24**	promethium 61 Pm [145]	**samarium** **62** **Sm** **150.36**	**europium** **63** **Eu** **151.96**	**gadolinium** **64** **Gd** **157.25**	terbium 65 Tb 158.93	**dysprosium** **66** **Dy** **162.50**	holmium 67 Ho 164.93	**erbium** **68** **Er** **167.26**	thulium 69 Tm 168.93	**ytterbium** **70** **Yb** **173.04**
* *Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	**uranium** **92** **U** **238.03**	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]
]

稳定同位素平衡分馏理论

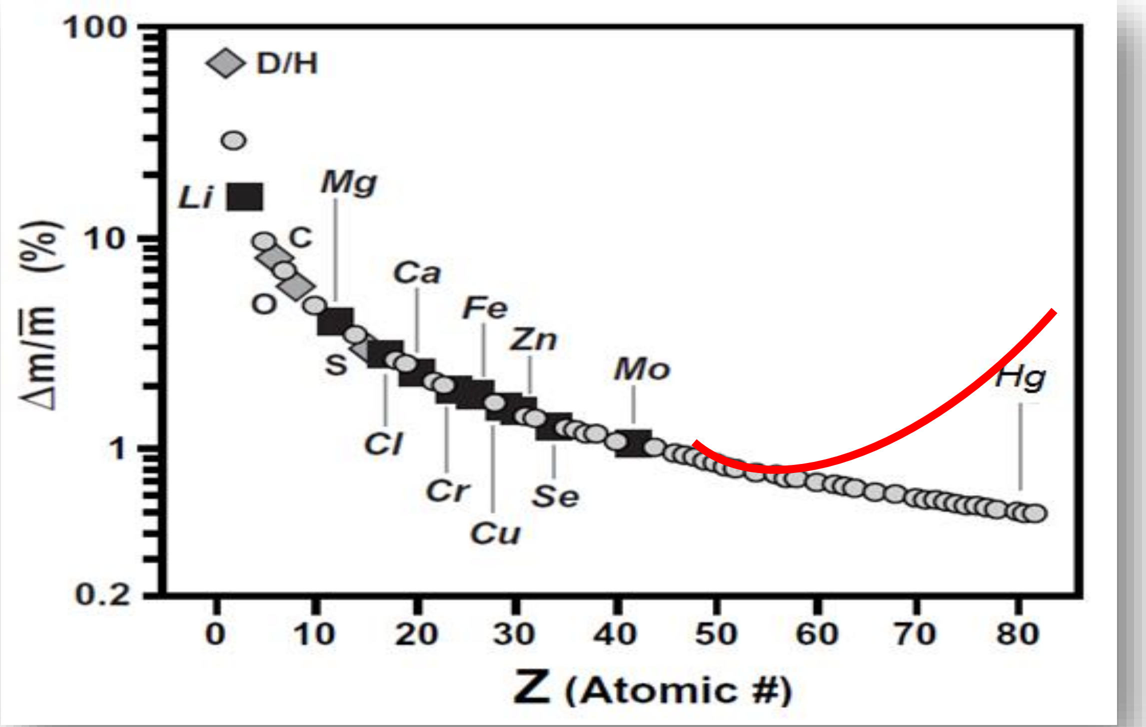


(Clark Johnson ,2004）

Bigeleisen-Mayer 高温近似式$\varepsilon \propto \Delta m/mm'T^2$

重元素质量大，相对质量差小，因此分馏很小

稳定同位素平衡分馏理论



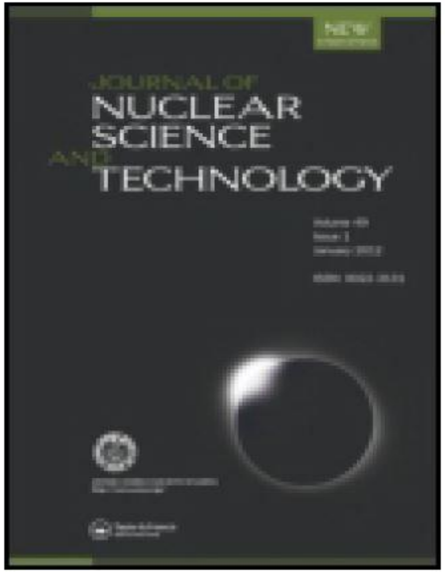
(Clark Johnson ,2004）

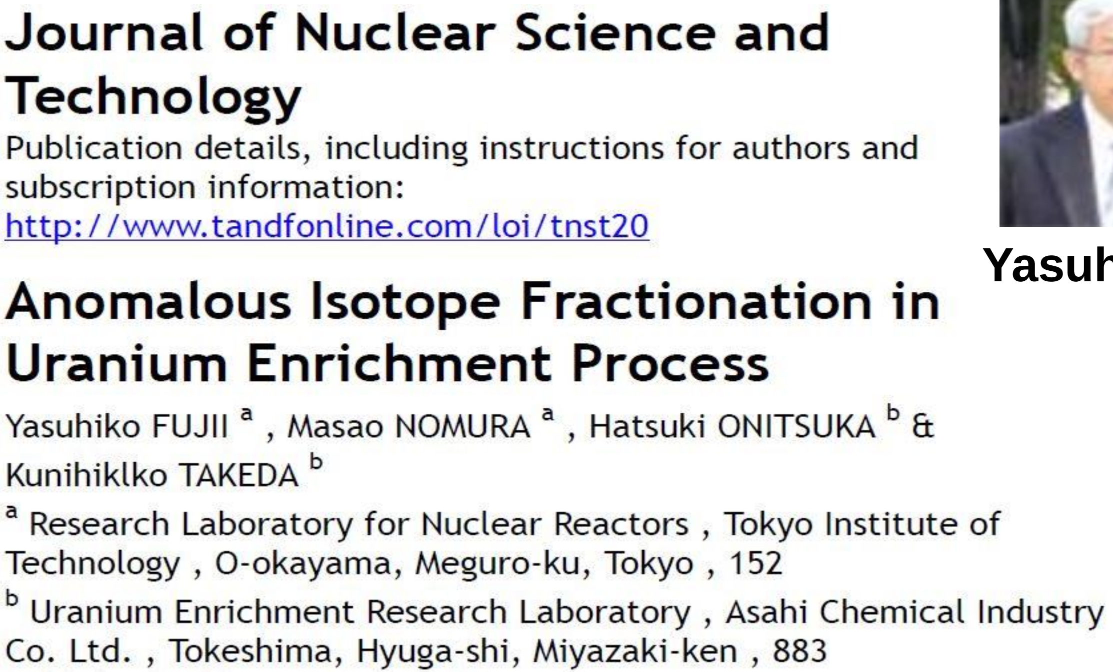
$$\ln\alpha = \ln\alpha_0 + \ln K_{anh} + \ln K_{BOELE} + \ln K_{hf} + \boxed{\ln K_{fs}}$$ （Bigeleisen,1996）

$\varepsilon \propto m/T$ ($Z_A > 40$)

核体积效应的发现

1989年，日本科学家首次发现核体积效应


JOURNAL OF NUCLEAR SCIENCE AND TECHNOLOGY


Journal of Nuclear Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tnst20

Anomalous Isotope Fractionation in Uranium Enrichment Process

Yasuhiko FUJII [a] , Masao NOMURA [a] , Hatsuki ONITSUKA [b] & Kunihiklko TAKEDA [b]

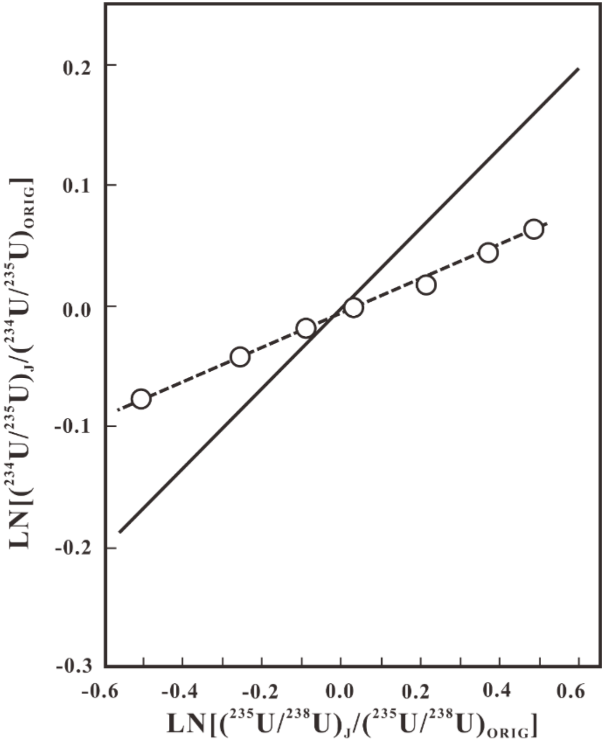
[a] Research Laboratory for Nuclear Reactors , Tokyo Institute of Technology , O-okayama, Meguro-ku, Tokyo , 152

[b] Uranium Enrichment Research Laboratory , Asahi Chemical Industry Co. Ltd. , Tokeshima, Hyuga-shi, Miyazaki-ken , 883


Yasuhiko Fujii

U同位素

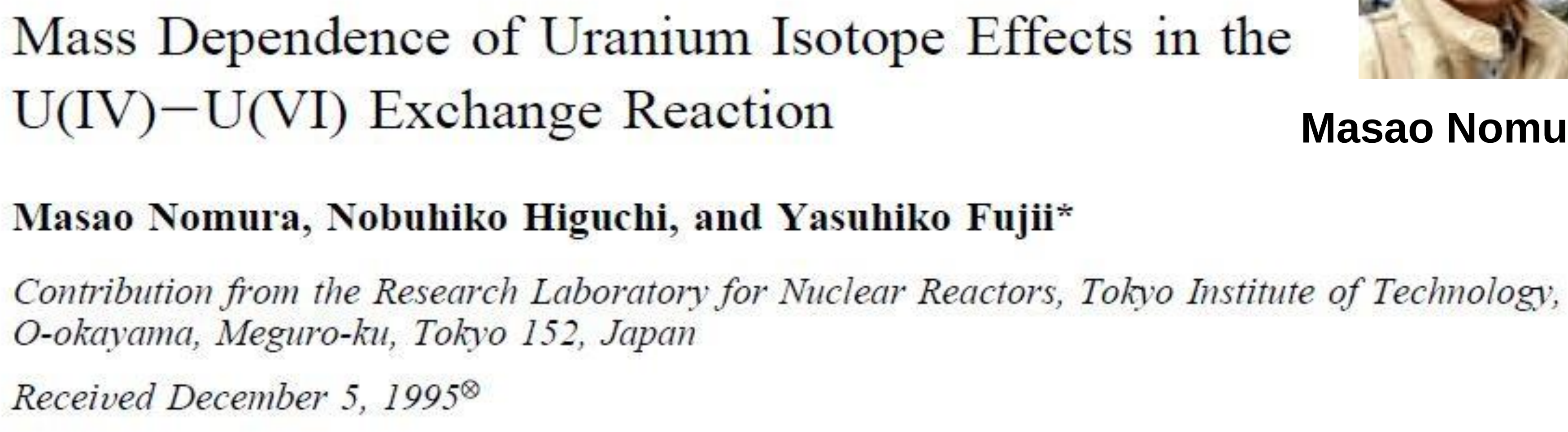
Yasuhiko Fujii



Fujii et al. (1989)

核体积效应的发现

1996年，Nomura等人发现^{233}U存在由核体积效应导致的异常同位素分馏



Mass Dependence of Uranium Isotope Effects in the U(IV)−U(VI) Exchange Reaction

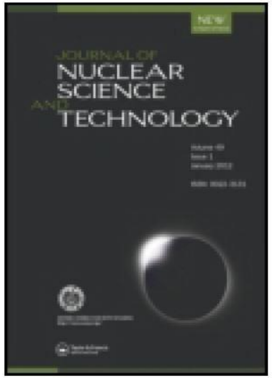
Masao Nomura, Nobuhiko Higuchi, and Yasuhiko Fujii*

Contribution from the Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

Received December 5, 1995⊗

Masao Nomura

核体积效应的发现



Journal of Nuclear Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tnst20

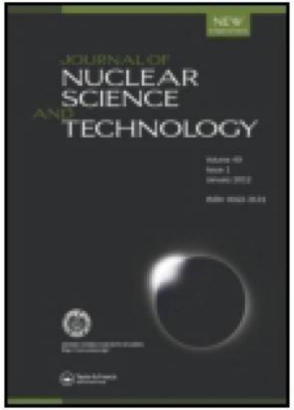
Gadolinium Isotope Separation by Cation Exchange Chromatography

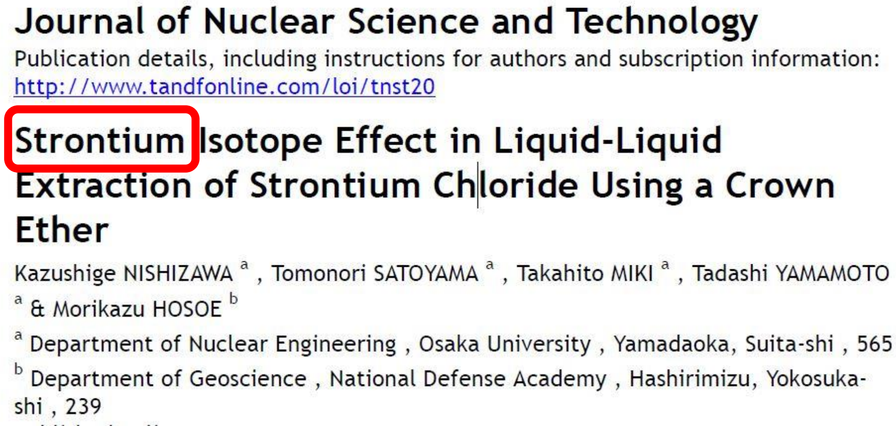
Jingren CHEN [a] , Masao NOMURA [b] , Yasuhiko FUJII [b] , Fumiaki KAWAKAMI [b] & Makoto OKAMOTO [b]

[a] Department of Modern Physics , Lanzhou University , Lanzhou , 730000 , P.R. China

[b] Research Laboratory for Nuclear Reactors , Tokyo Institute of

1992年，Chen等人在液液萃取实验中发现^{157}Gd的异常分馏





Journal of Nuclear Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tnst20

Strontium Isotope Effect in Liquid-Liquid Extraction of Strontium Chloride Using a Crown Ether

Kazushige NISHIZAWA [a] , Tomonori SATOYAMA [a] , Takahito MIKI [a] , Tadashi YAMAMOTO [a] & Morikazu HOSOE [b]

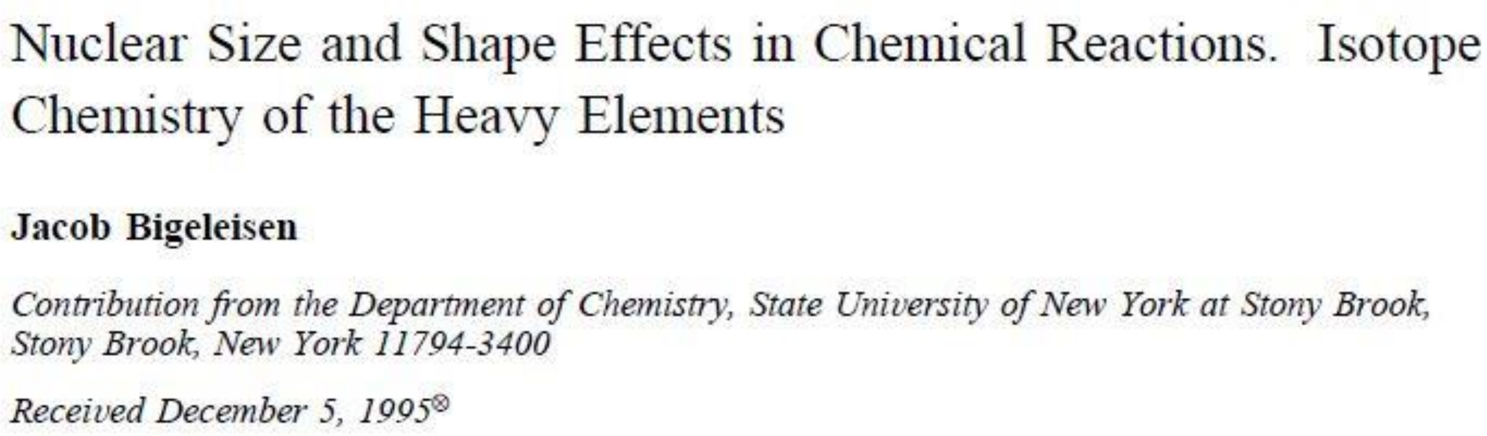
[a] Department of Nuclear Engineering , Osaka University , Yamadaoka, Suita-shi , 565

[b] Department of Geoscience , National Defense Academy , Hashirimizu, Yokosuka-shi , 239

1995年，Nishizawa等人在液液萃取实验中发现^{87}Sr的异常分馏

核体积效应的首次理论研究

1996年，Bigeleisen修正了同位素的平衡分馏公式



Nuclear Size and Shape Effects in Chemical Reactions. Isotope Chemistry of the Heavy Elements

Jacob Bigeleisen

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400

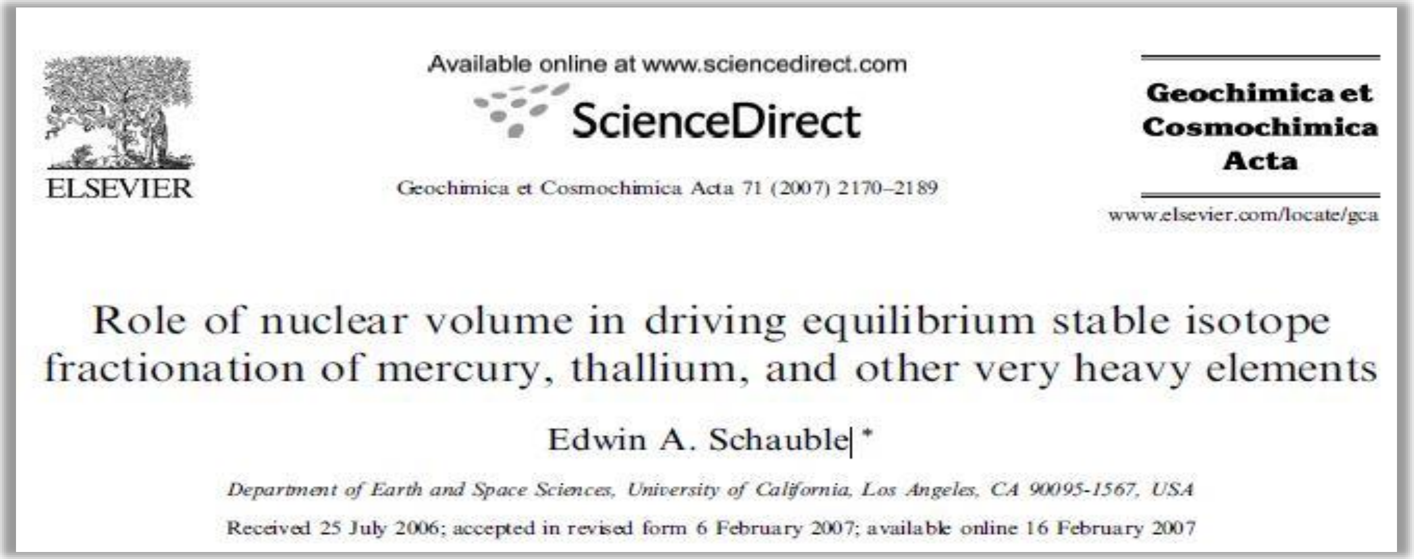
Received December 5, 1995®

Jacob Bigeleisen

$$\ln\alpha = \ln\alpha_0 + \ln K_{anh} + \ln K_{BOELE} + \ln K_{hf} + \boxed{\ln K_{fs}}$$

核体积效应在地球化学领域的首次研究

2007年，Schauble首次理论上预测了Hg、Tl等重同位素体系的核体积效应分馏大小



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ScienceDirect

Geochimica et Cosmochimica Acta 71 (2007) 2170–2189

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

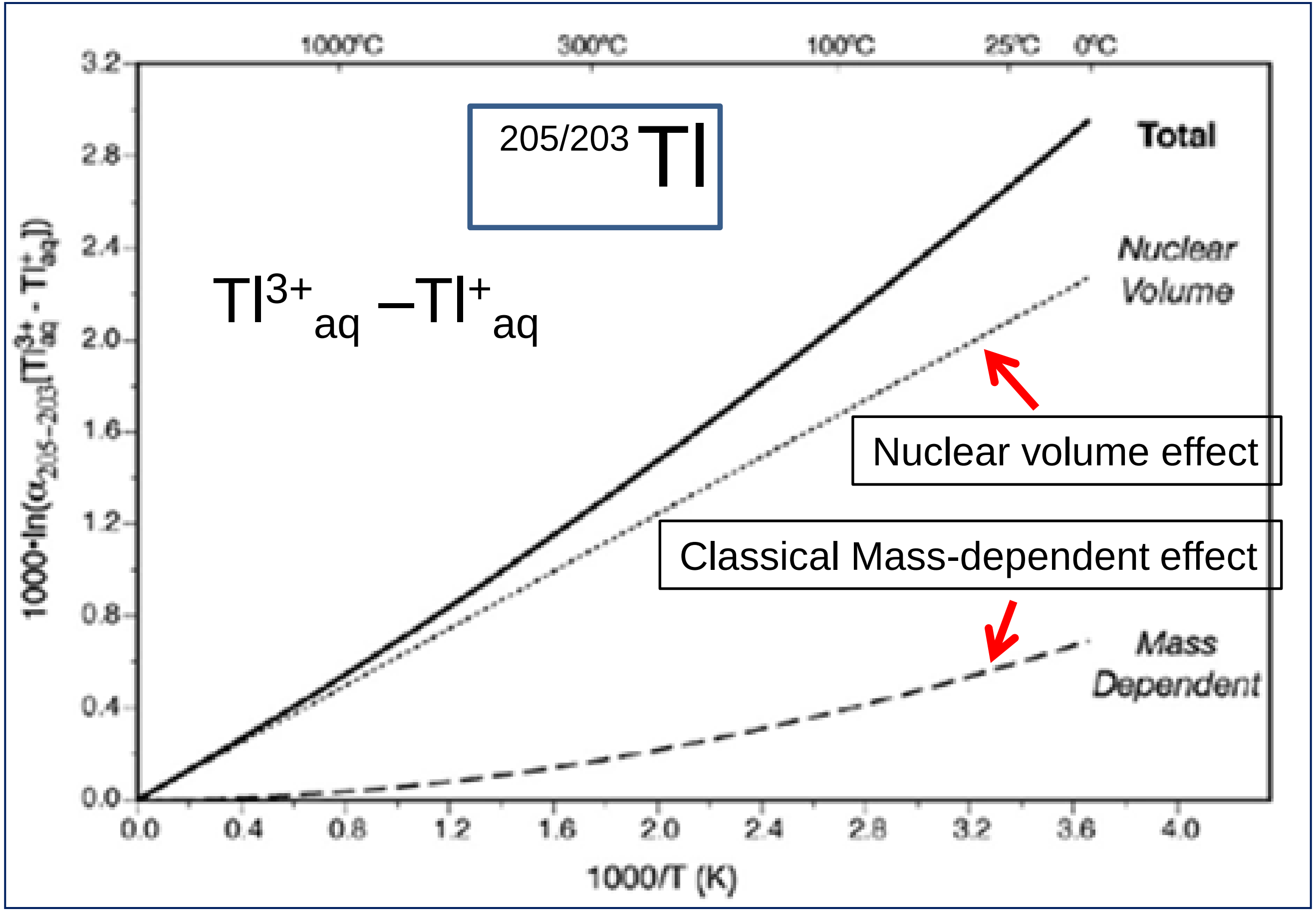
Role of nuclear volume in driving equilibrium stable isotope fractionation of mercury, thallium, and other very heavy elements

Edwin A. Schauble *

Department of Earth and Space Sciences, University of California, Los Angeles, CA 90095-1567, USA

Received 25 July 2006; accepted in revised form 6 February 2007; available online 16 February 2007

Edwin A. Schauble

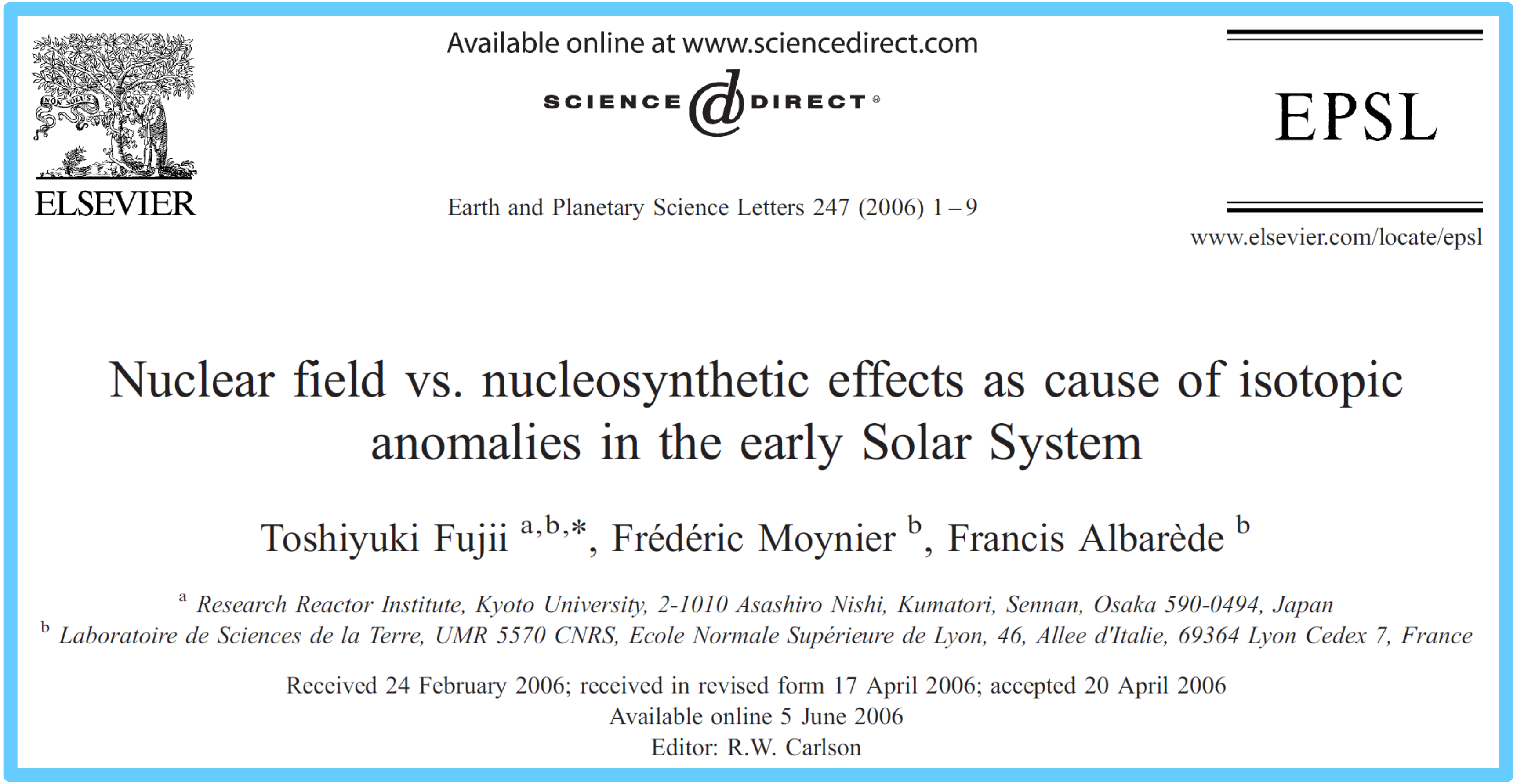


$^{205/203}$Tl

Tl^{3+}_{aq} –Tl^{+}_{aq}

Nuclear volume effect

Classical Mass-dependent effect



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Earth and Planetary Science Letters 247 (2006) 1 – 9

EPSL
www.elsevier.com/locate/epsl

Nuclear field vs. nucleosynthetic effects as cause of isotopic anomalies in the early Solar System

Toshiyuki Fujii [a,b,*], Frédéric Moynier [b], Francis Albarède [b]

[a] Research Reactor Institute, Kyoto University, 2-1010 Asashiro Nishi, Kumatori, Sennan, Osaka 590-0494, Japan
[b] Laboratoire de Sciences de la Terre, UMR 5570 CNRS, Ecole Normale Supérieure de Lyon, 46, Allee d'Italie, 69364 Lyon Cedex 7, France

Received 24 February 2006; received in revised form 17 April 2006; accepted 20 April 2006
Available online 5 June 2006
Editor: R.W. Carlson

Fujii et al. (2006, EPSL)

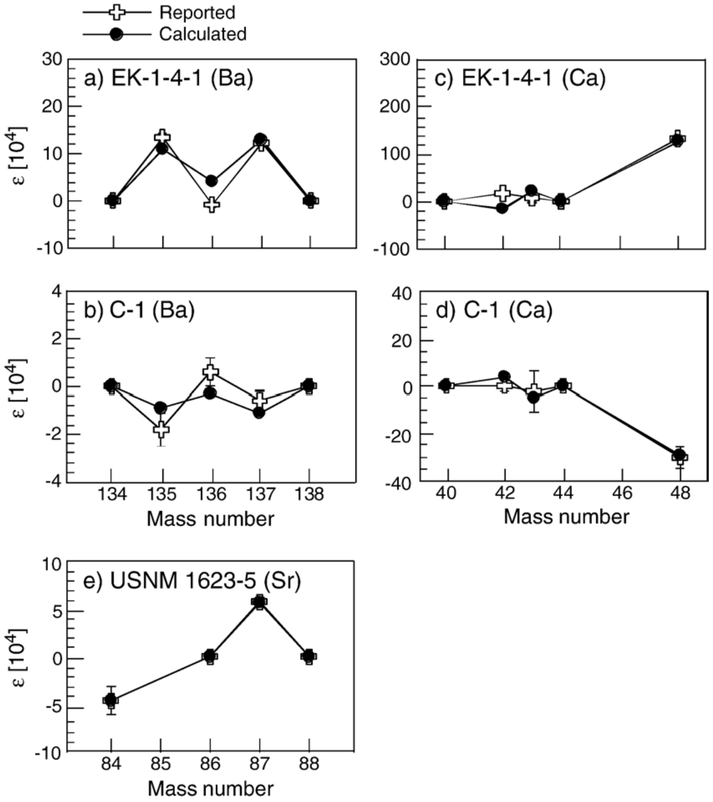
真正的首次研究： 2006年 Fujii

Toshiyuki Fujii

$$ln\alpha = \delta\langle r^2\rangle_{m,m'} \times a + \frac{\delta m}{mm'} \times b$$

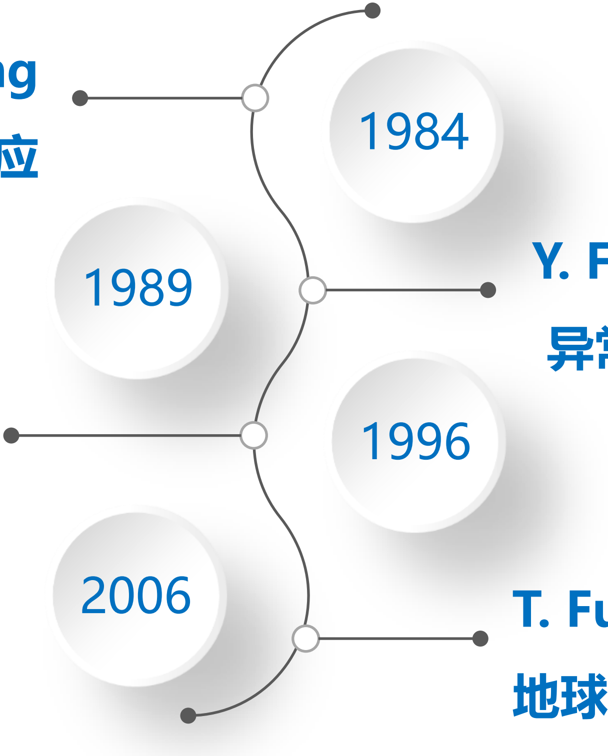
$$\varepsilon_{m_i} = \left(\delta\langle r^2\rangle_{m_1,m_i} - \frac{m_2(m_i-m_1)}{m_i(m_2-m_1)}\delta\langle r^2\rangle_{m_1,m_2}\right) \times a$$

$$a \propto \frac{1}{T};\ b \propto \frac{1}{T^2}$$



Fujii et al. (2006, EPSL)

核体积效应发展历程



1984

W. H. King

定义核体积效应

1989

Y. Fujii

异常U同位素分馏

1996

Bigeleisen

B-M公式修正

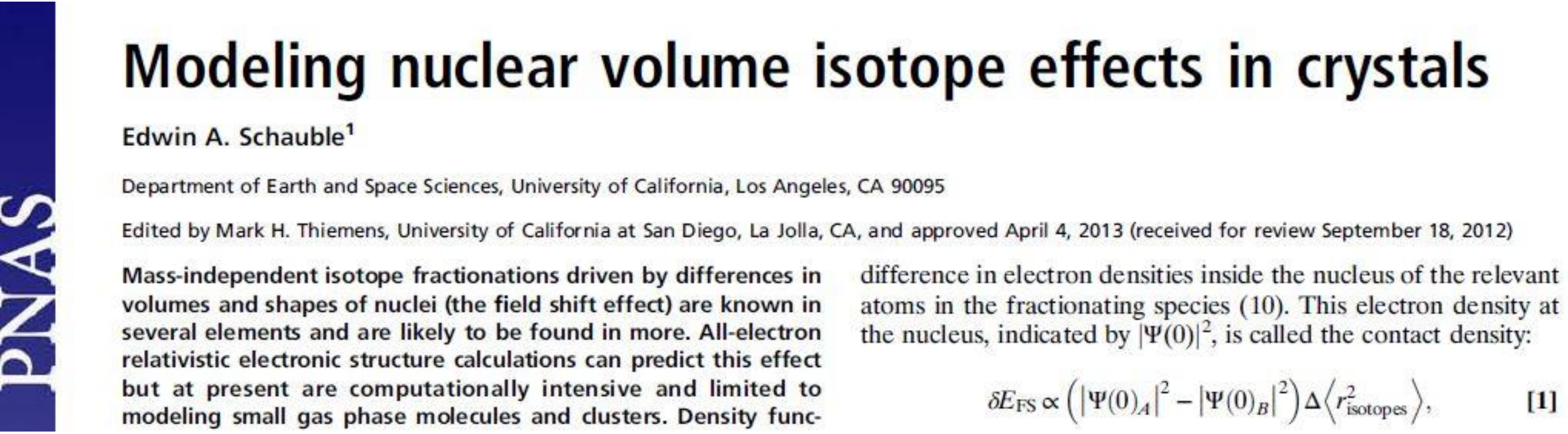
2006

T. Fujii

地球化学领域首次NVE理论研究

核体积效应在固体体系首次理论研究

2013年，Schauble首次对重同位素*固体*体系的核体积效应进行了理论计算研究



Modeling nuclear volume isotope effects in crystals

Edwin A. Schauble[1]

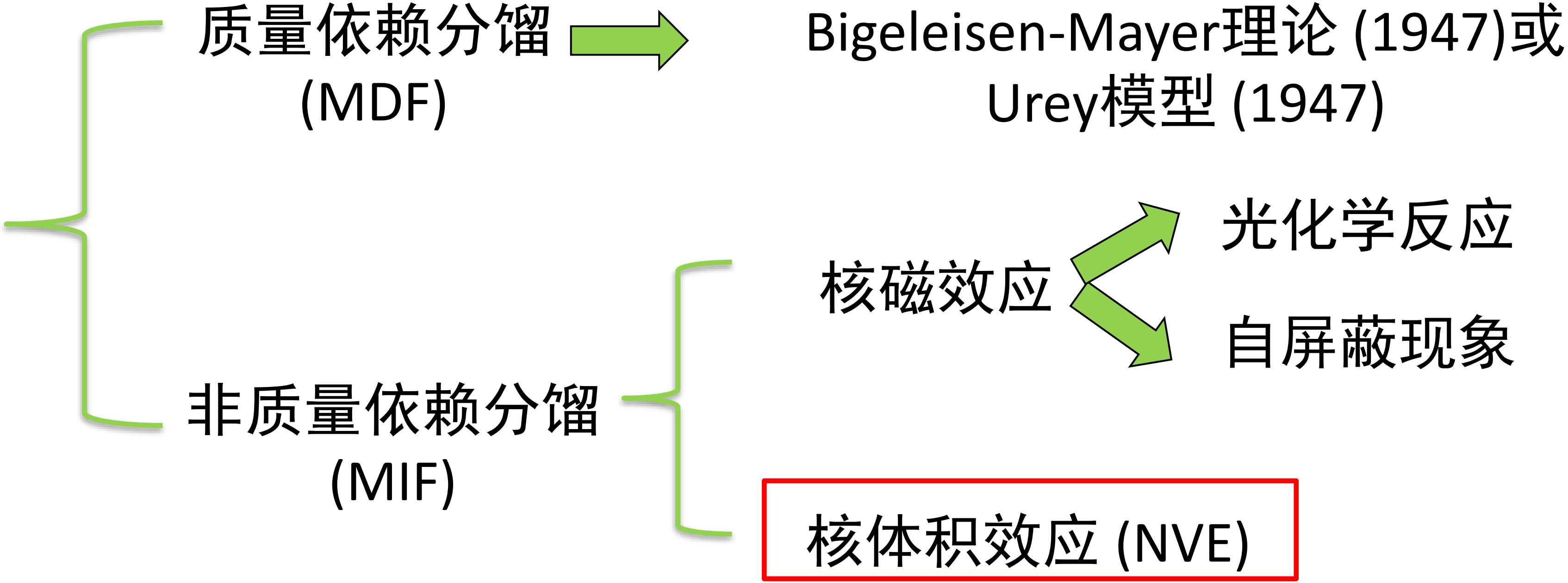
Department of Earth and Space Sciences, University of California, Los Angeles, CA 90095

Edited by Mark H. Thiemens, University of California at San Diego, La Jolla, CA, and approved April 4, 2013 (received for review September 18, 2012)

Mass-independent isotope fractionations driven by differences in volumes and shapes of nuclei (the field shift effect) are known in several elements and are likely to be found in more. All-electron relativistic electronic structure calculations can predict this effect but at present are computationally intensive and limited to modeling small gas phase molecules and clusters. Density func-

difference in electron densities inside the nucleus of the relevant atoms in the fractionating species (10). This electron density at the nucleus, indicated by $|\Psi(0)|^2$, is called the contact density:

$$\delta E_{\mathrm{FS}} \propto \left(|\Psi(0)_A|^2 - |\Psi(0)_B|^2\right)\Delta\left\langle r^2_{\mathrm{isotopes}}\right\rangle, \qquad [1]$$



质量依赖分馏
(MDF)

Bigeleisen-Mayer理论 (1947)或
Urey模型 (1947)

非质量依赖分馏
(MIF)

核磁效应

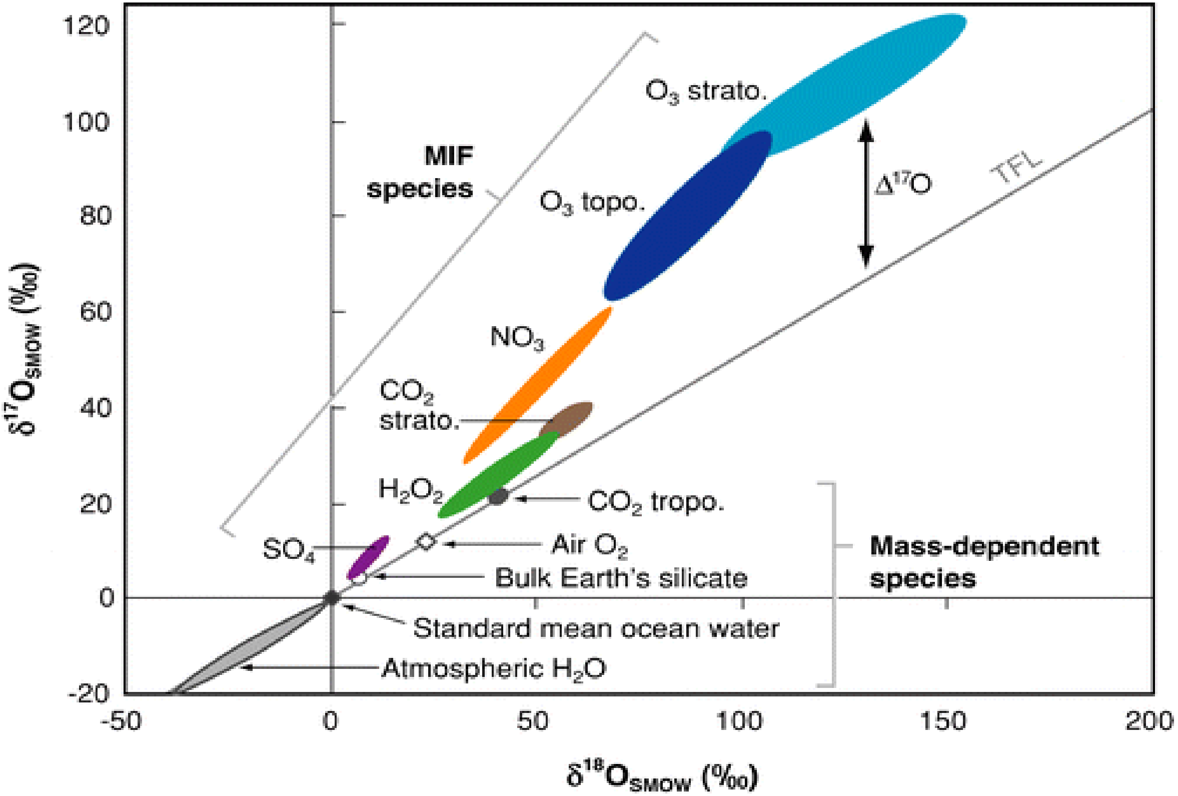
光化学反应

自屏蔽现象

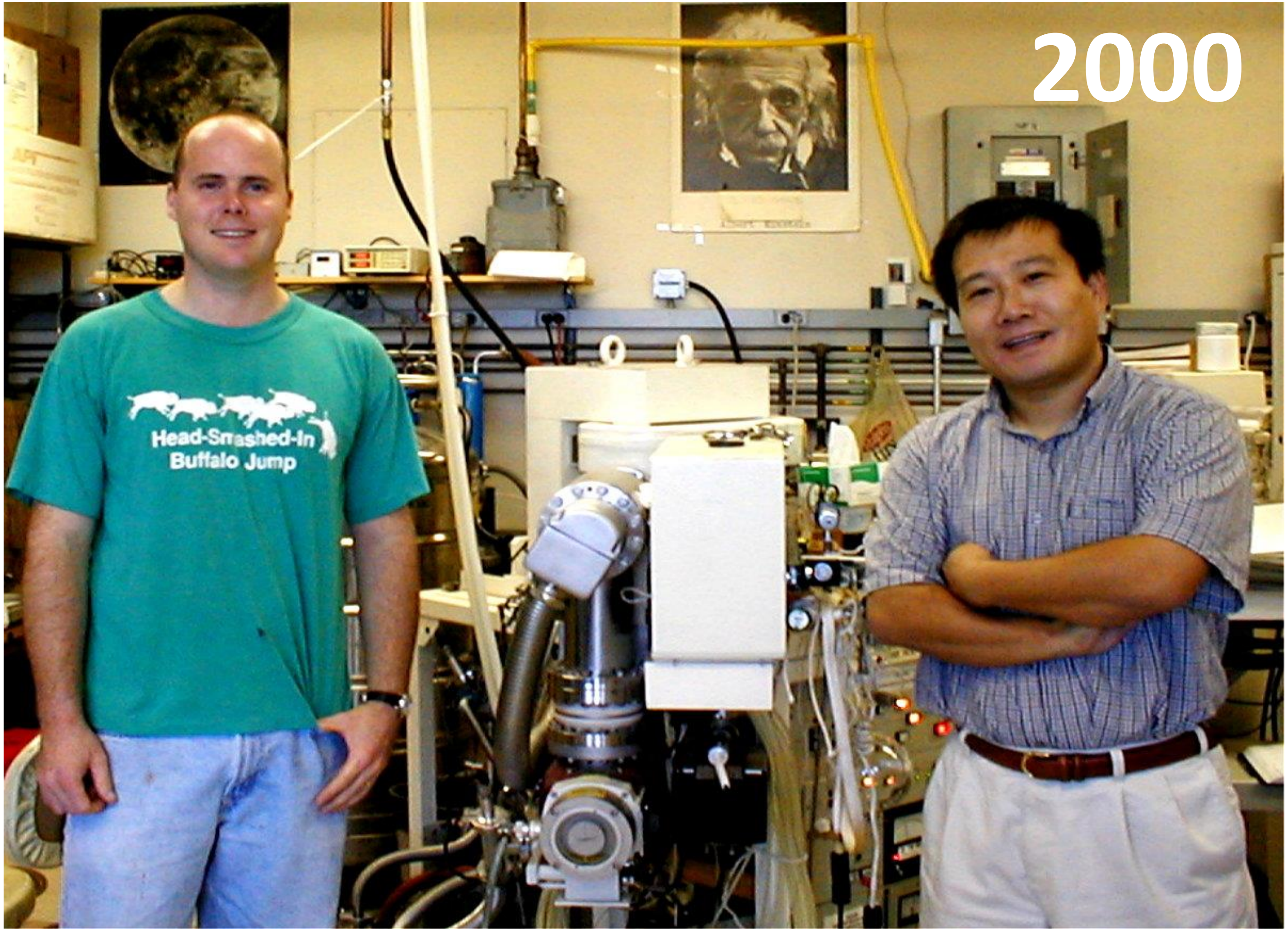
核体积效应 (NVE)

$$\Delta^{17}O = \delta^{17}O - 0.52 * \delta^{18}O$$

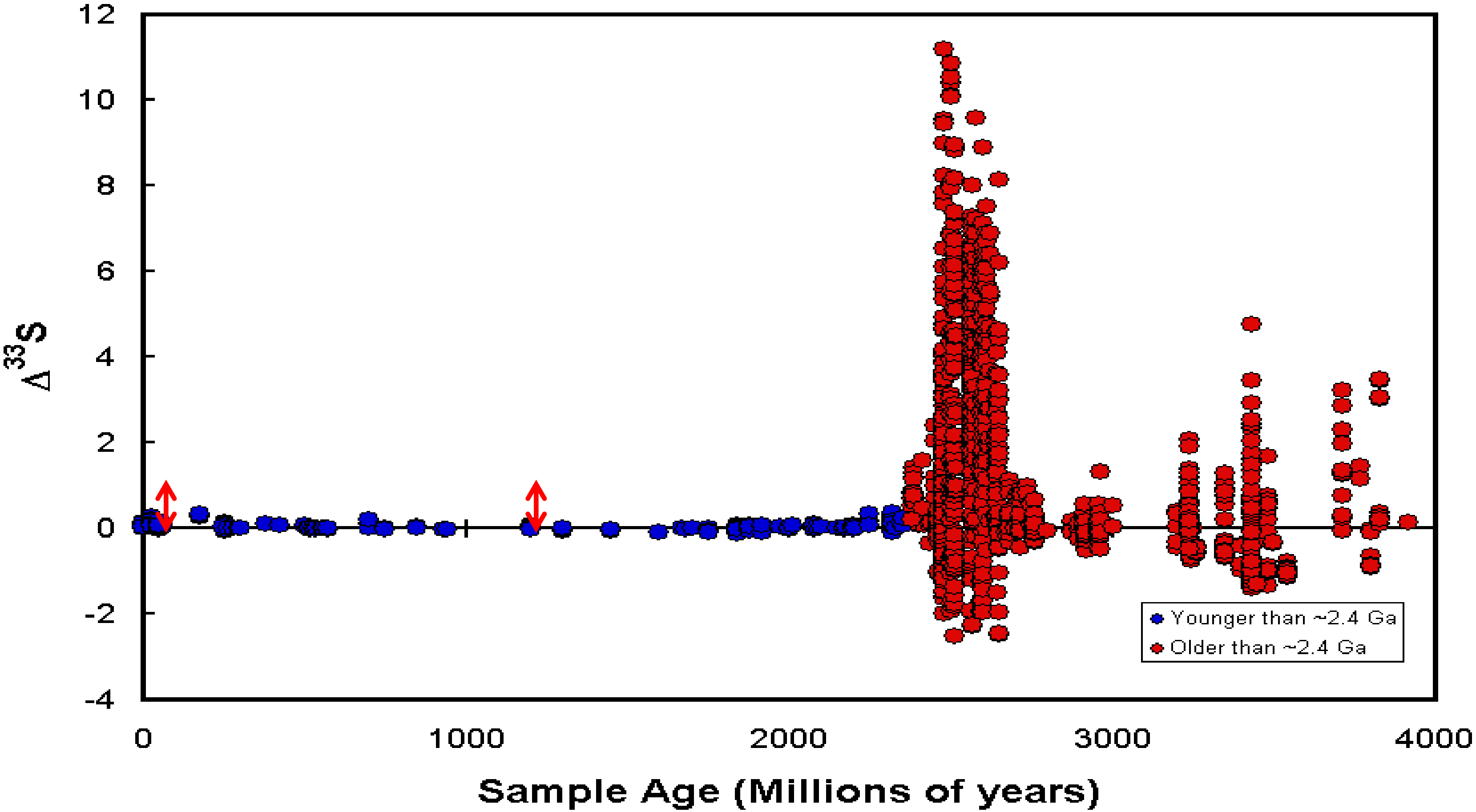
Mark Thiemens

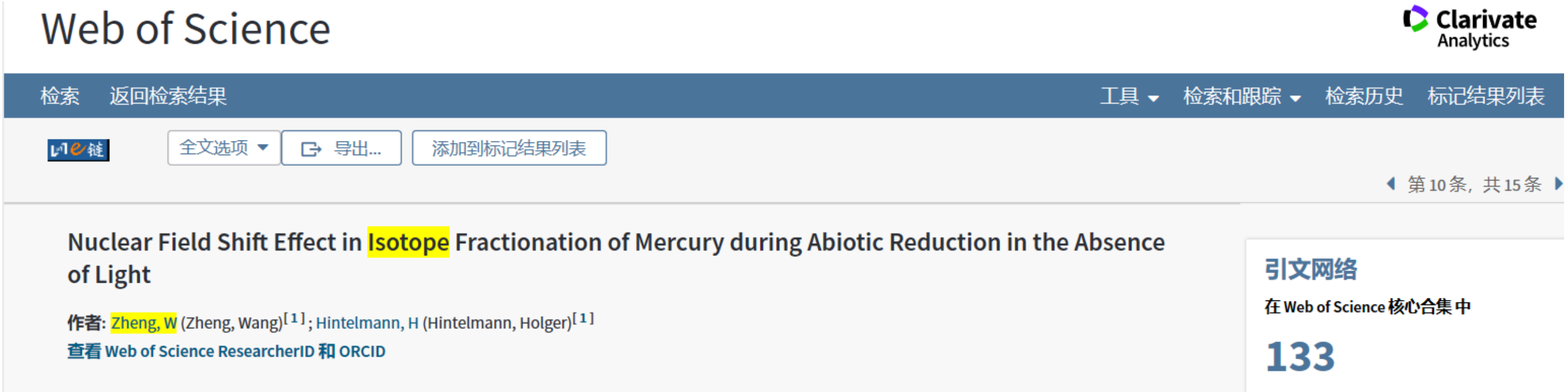


Thiemens MH. 2006.
Annu. Rev. Earth Planet. Sci. 34:217–62



2000
Head-Smashed-In
Buffalo Jump


12
10
8
6
4
2
0
-2
-4
$\Delta^{33}S$
0
1000
2000
3000
4000
Sample Age (Millions of years)
● Younger than ~2.4 Ga
● Older than ~2.4 Ga



Nuclear Field Shift Effect in Isotope Fractionation of Mercury during Abiotic Reduction in the Absence of Light

作者: Zheng, W (Zheng, Wang)[1]; Hintelmann, H (Hintelmann, Holger)[1]
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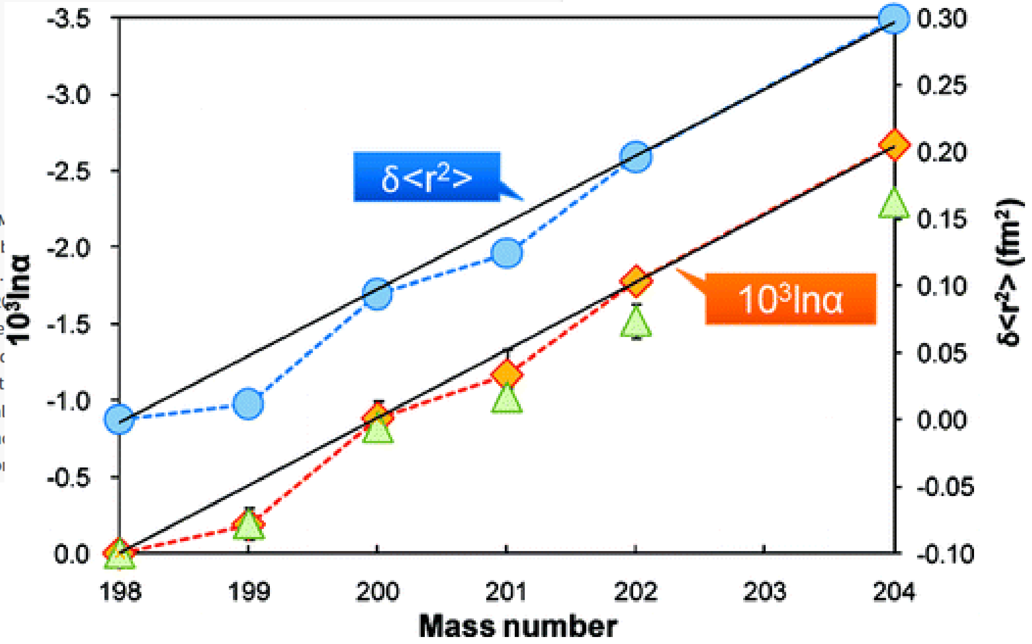
引文网络
在 Web of Science 核心合集中
133

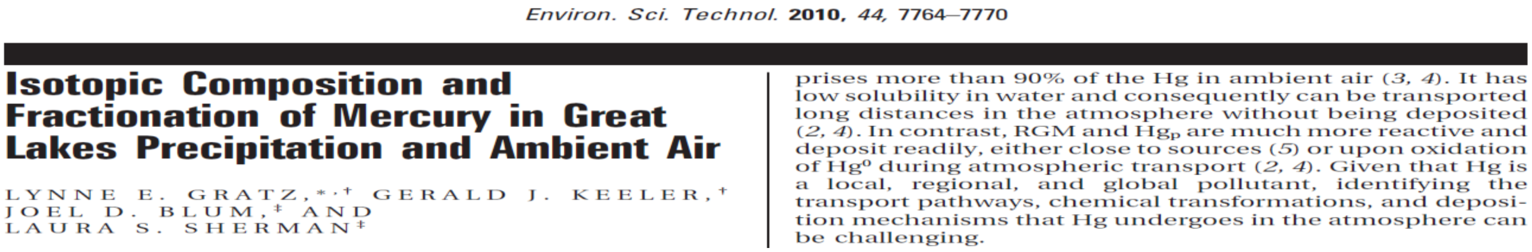
JOURNAL OF PHYSICAL CHEMISTRY A
卷: 114 **期:** 12 **页:** 4238-4245
DOI: 10.1021/jp910353y
出版年: APR 1 2010
文献类型: Article
查看期刊影响力

摘要

We investigated the abiotic reduction of inorganic Hg(II) by dissolved organic matter (DOM
quantified fractionation of Hg isotopes during these processes. The kinetics of reduction
reactions, implying different reactive Hg(II) species resulting from Hg-DOM complexation.
reduction by both reducing reagents, Isotopes with odd atomic masses (Hg-199 and Hg-2
mass dependent fractionation process. the fractionation factors (alpha) showed an odd-e
charge radii. We demonstrated that these isotopic anomalies originated from nuclear fiel
fractionation factors was estimated and found to be as significant as the mass dependent
explained by NFS and determined to be between 1.5 and 1.6 in abiotic nonphotochemical
photochemical reduction. Therefore, we first demonstrated experimentally the significan
showed the application of isolope fractionation to distinguish between different reductio



Hg的非质量分馏(MIF)

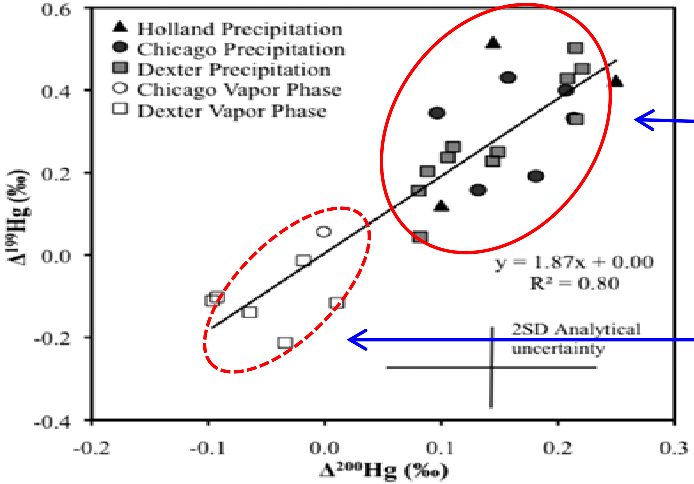


Environ. Sci. Technol. **2010,** *44,* 7764–7770

Isotopic Composition and Fractionation of Mercury in Great Lakes Precipitation and Ambient Air

LYNNE E. GRATZ,*,† GERALD J. KEELER,†
JOEL D. BLUM,‡ AND
LAURA S. SHERMAN‡

prises more than 90% of the Hg in ambient air (*3, 4*). It has low solubility in water and consequently can be transported long distances in the atmosphere without being deposited (*2, 4*). In contrast, RGM and Hg_p are much more reactive and deposit readily, either close to sources (*5*) or upon oxidation of Hg^0 during atmospheric transport (*2, 4*). Given that Hg is a local, regional, and global pollutant, identifying the transport pathways, chemical transformations, and deposition mechanisms that Hg undergoes in the atmosphere can be challenging.



沉淀
Δ^{199}Hg=0.04~0.52
Δ^{200}Hg=0.25 (最大）

气相
Δ^{199}Hg=-0.21~0.06
Δ^{200}Hg=-0.04 (平均）

Gratz et al., Environ. Sci. Technol., 2010

Available online at www.sciencedirect.com

SciVerse ScienceDirect

Geochimica et Cosmochimica Acta 90 (2012) 33–46

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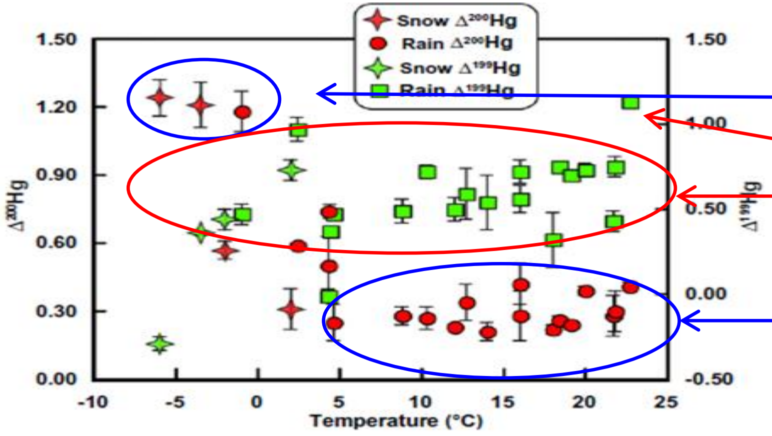
Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Unusual fractionation of both odd and even mercury isotopes in precipitation from Peterborough, ON, Canada

JiuBin Chen [a,b,*], Holger Hintelmann [b], XinBin Feng [a], Brian Dimock [b]

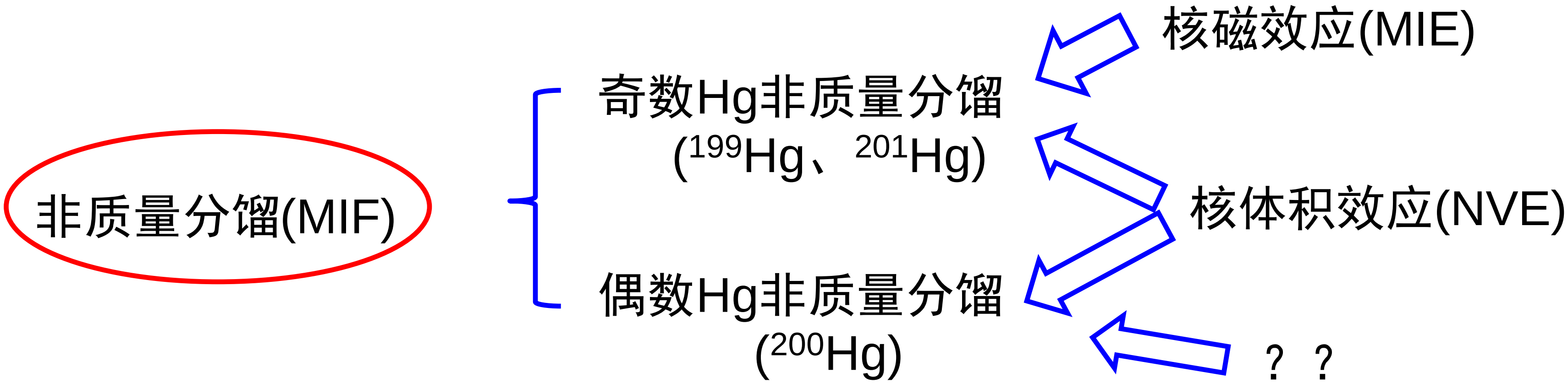


Δ^{200}Hg=1.24

Δ^{199}Hg=1.13 (最大)

Δ^{200}Hg=0.25

Chen et al., GCA, 2012



非质量分馏(MIF)

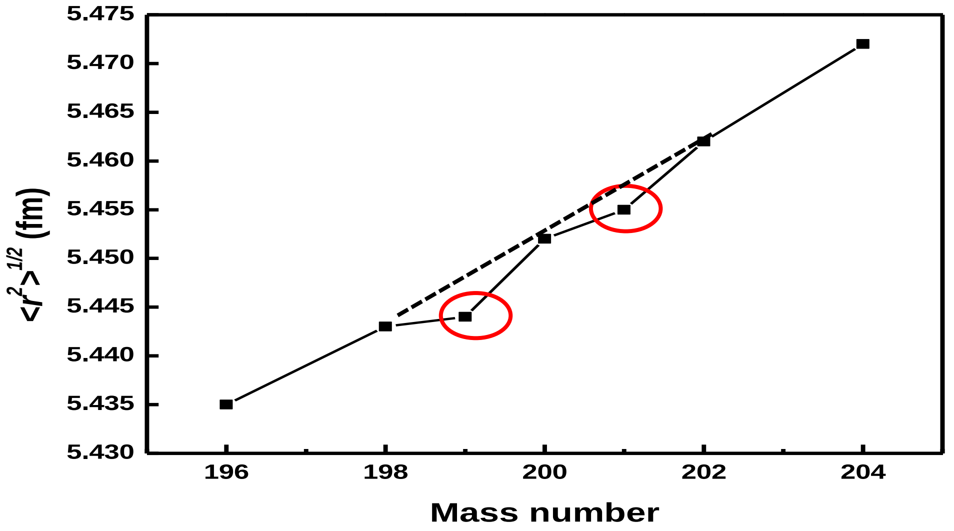
奇数Hg非质量分馏 (^{199}Hg、^{201}Hg)

偶数Hg非质量分馏 (^{200}Hg)

核磁效应(MIE)

核体积效应(NVE)

？？



Root mean square nuclear charge radii($<r^2>^{1/2}$)
of mercury isotopes (Fricke G. & Heilig K., 2004)

计算方法

Method Ⅰ

电子能计算

$$\ln K_{fs} = (kT)^{-1}\{[\underline{E^0(A'X) - E^0(AX)}] - [E^0(A'Y) - E^0(AY)]\}$$

电子密度计算

$$\ln K_{fs} = (kT)^{-1}\{Z_A e^2/6\varepsilon_0 \underline{[\bar{\rho}_e^A(AX) - \bar{\rho}_e^A(AY)}]\delta\langle r^2\rangle_{AA'}\}$$

Method Ⅱ

重金属元素需要处理其“相对论效应”

- 经典量子化学
- 求解Schrödinger方程

- 相对论量子化学
- 求解DIRAC方程

相对论效应

- 旋-轨耦合效应，使简并轨道发生能级分裂；
- 直接相对论效应，导致内层轨道收缩；
- 间接相对论效应，导致外层轨道膨胀。

(Pyykkö, 1988)

国内外相关研究

DIRAC

Schauble(2007，2013)：

Hg、Tl、Sn

DIRAC

Wiederhold(2010)：

Hg

GRASP2K

M Abe(2008-2010):

U

UTCHEM

T Fujii(2010-2019)：

Zn、Ni、Pb、Tl …

IODKH-IOSO-MFSO

Nemoto(2015)

U

Yang & Liu (2015-2016)

Fang & Liu (2019)

DIRAC & ADF

Hg、Tl、Pb、U、Sn、W

我们建立的方法

Methods 1

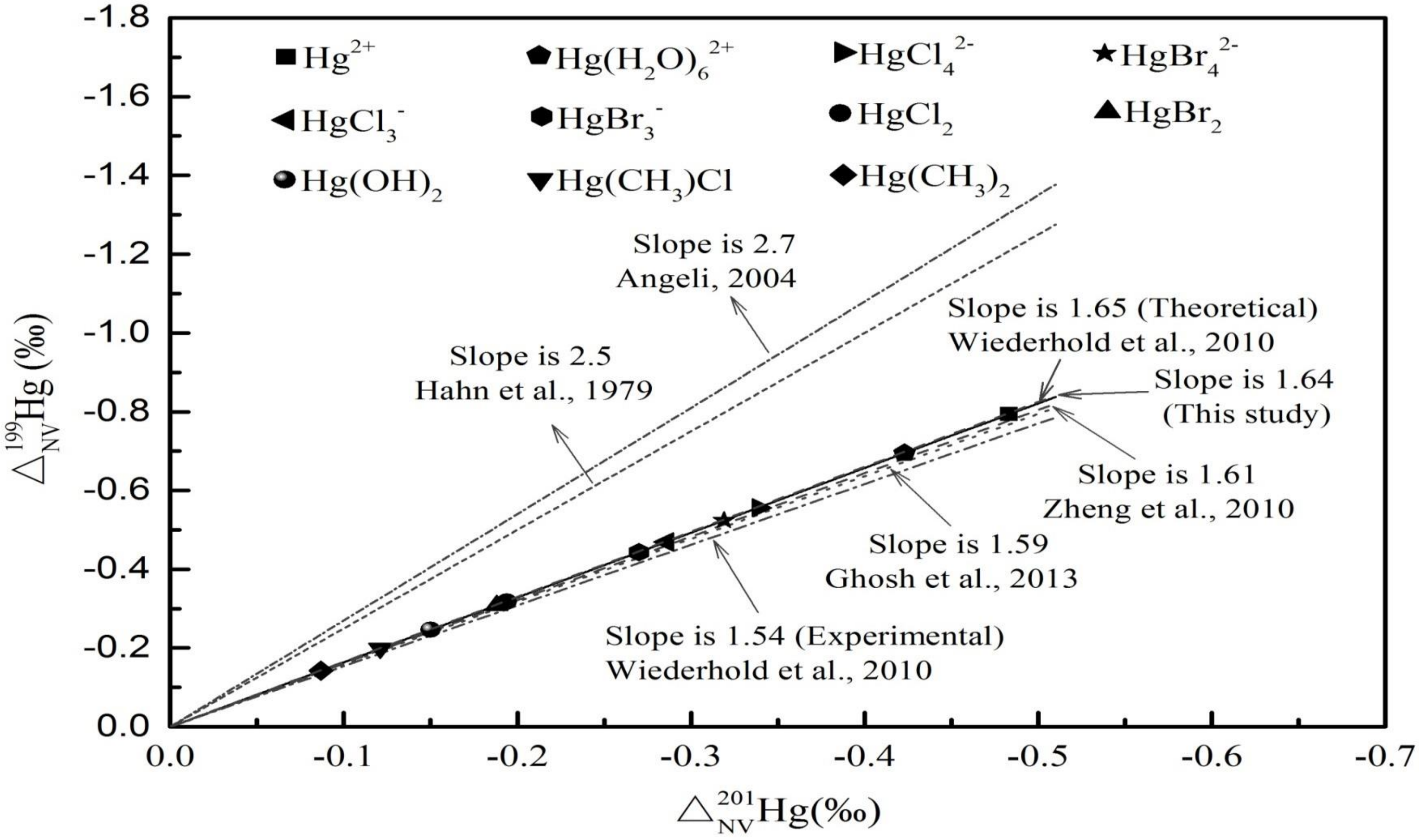
对小体系：

- ✓ Relativistic electronic structures with four-component wave functions
- ✓ Software package：Dirac13.1
- ✓ All-electron, Dirac-Hartree-Fock (DHF) Theory
- ✓ Gaussian exponent ξ ： ξ=3/(2<r^2>)
- ✓ Calculate systems with less than 20 atoms

Methods 2

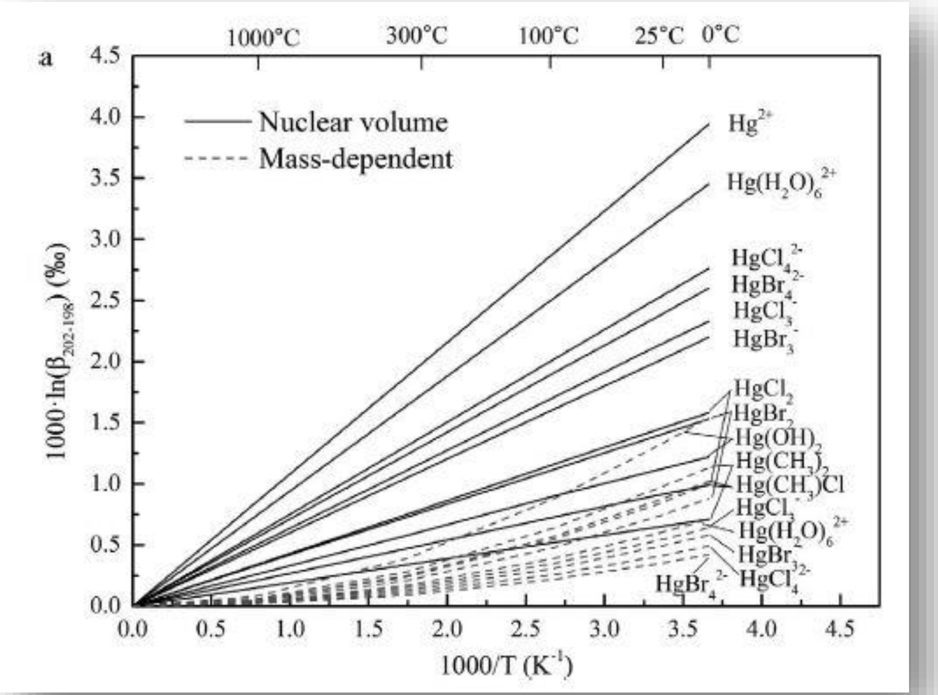
对固体和大体系：

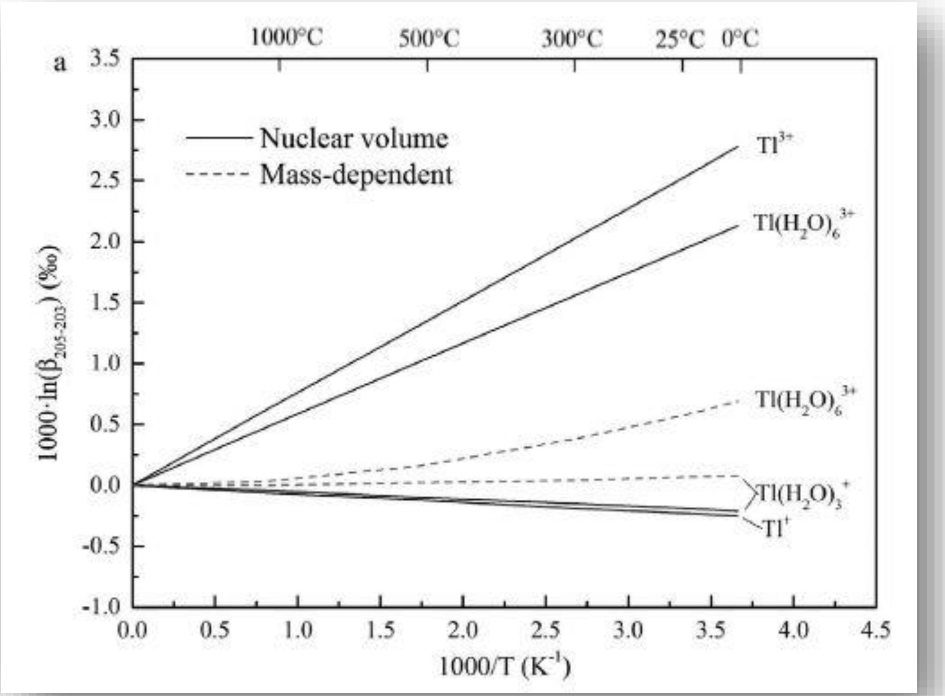
- ✓ Relativistic effects ： Scalar relativistic effects （ZORA)
- ✓ Software package：ADF（ADF module，BAND module）
- ✓ All-electron，Density Functional Theory （DFT)
- ✓ **Kinetic Isotope Effects (KIEs)**



(Yang and Liu, 2015)

Method Ⅰ

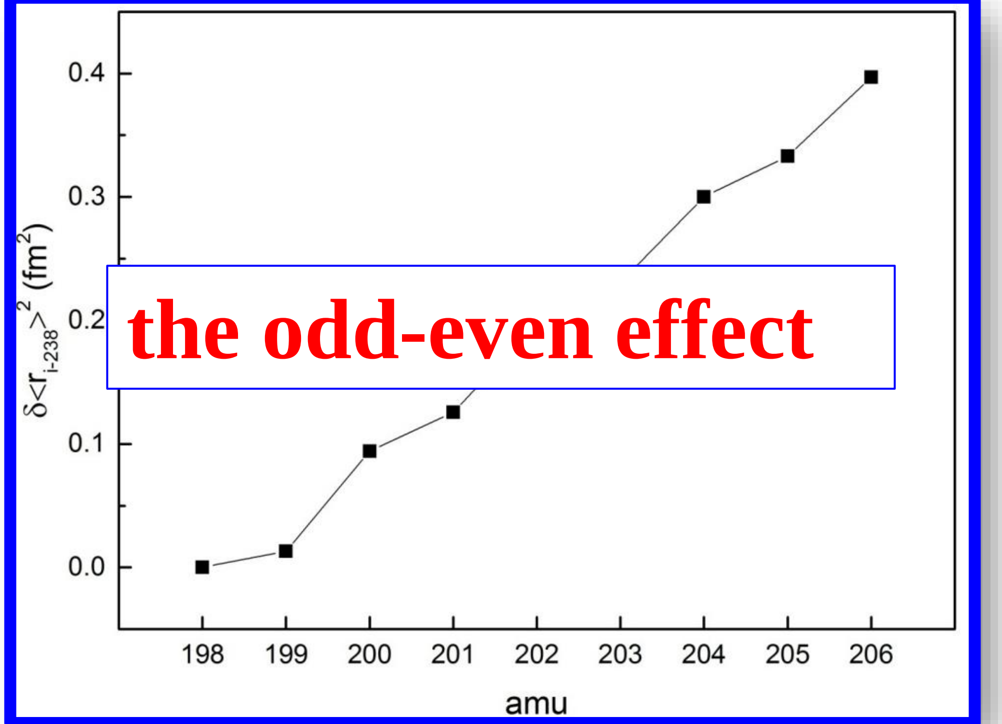




(Yang & Liu, 2015)

我们对固体计算方法的改进

$$\ln K_{fs} = (kT)^{-1}\{Z_A e^2/6\varepsilon_0[\bar{\rho}_e^A(AX) - \bar{\rho}_e^A(AY)]\delta\langle r^2\rangle_{AA'}$$



the odd-even effect

Method Ⅱ

$\bar{\rho}_e^A(AX) - \bar{\rho}_e^A(AY)$ ——在核的有效电子密度之差

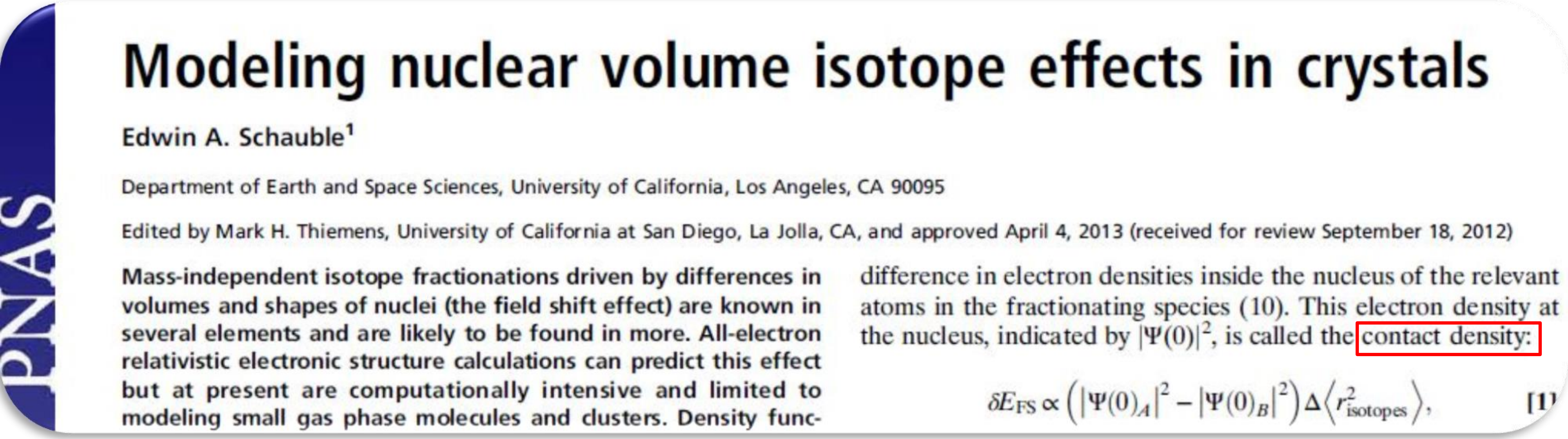
在核电子密度：

effective density ——有效电子密度。它是计算原子核中心周围一定范围内电子密度。

contact density ——接触电子密度。它是代表原子核位置r=0的点上的电子密度，它是有效电子密度的一种近似。

但对于重元素来说，这种近似会造成10%的误差。

Method Ⅱ



Modeling nuclear volume isotope effects in crystals

Edwin A. Schauble[1]

Department of Earth and Space Sciences, University of California, Los Angeles, CA 90095

Edited by Mark H. Thiemens, University of California at San Diego, La Jolla, CA, and approved April 4, 2013 (received for review September 18, 2012)

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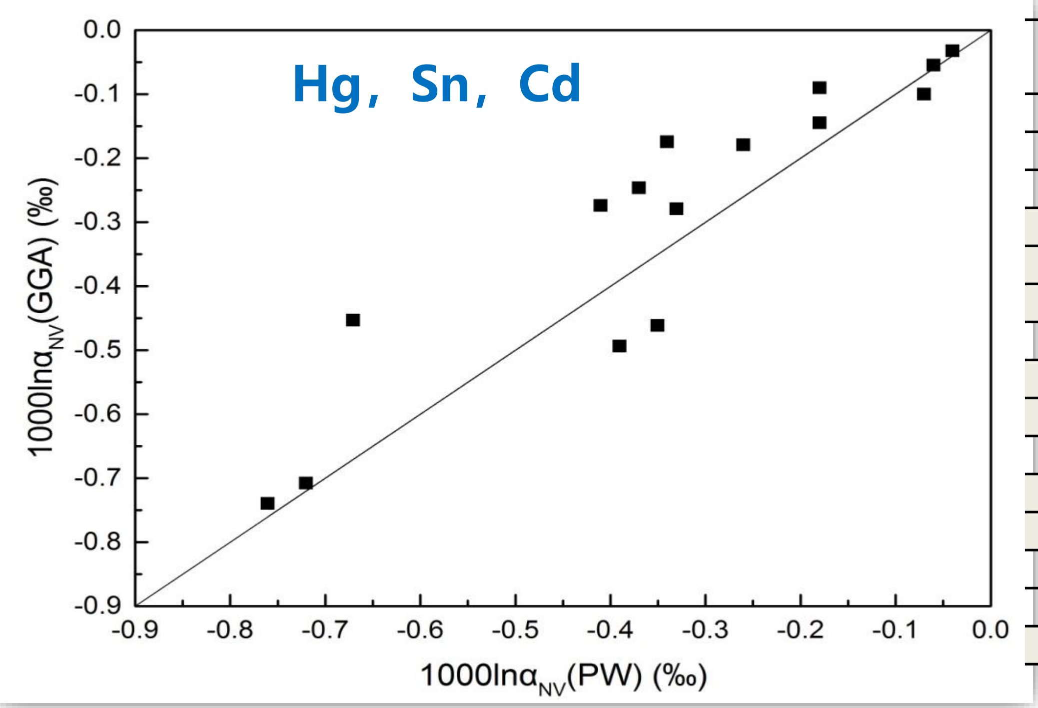
$$\delta E_{FS} \propto \left(|\Psi(0)_A|^2 - |\Psi(0)_B|^2\right)\Delta\left\langle r^2_{\text{isotopes}}\right\rangle, \qquad [1]$$

Software: ABINIT
Method: DFT-PAW

Method Ⅱ



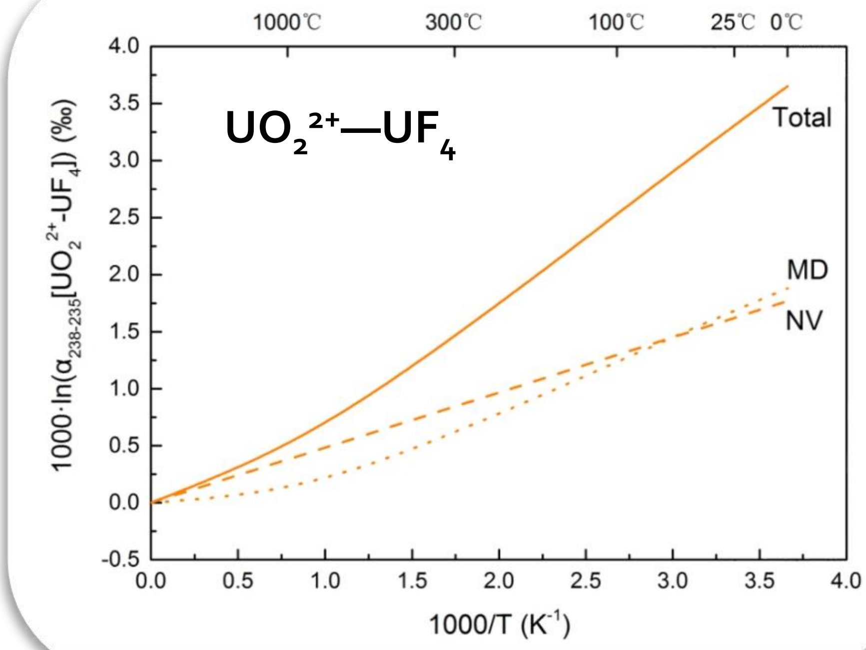
	PAW(Schauble, 2013)	GGA-PBE-TZ2P
HgS-HgO	-0.26033	-0.17887
Hg2Cl2-HgO	-0.33041	-0.27881
Hg2Cl2-HgS	-0.07008	-0.09994
aHg-Hg2Cl2	-0.34031	-0.1741
aHg-HgO	-0.67071	-0.45291
aHg-HgS	-0.41038	-0.27404
CdS-CdO	-0.06002	-0.05479
aCd-CdS	-0.18005	-0.09012
aCd-CdO	-0.18005	-0.14492
SnO2-SnF4	-0.04003	-0.03191
aSn-SnF4	-0.39026	-0.49347
aSn-SnO2	-0.35023	-0.46156
SnCl2-SnF4	-0.76037	-0.73947
SnCl2-SnO2	-0.72034	-0.70757
SnCl2-aSn	-0.37011	-0.24601

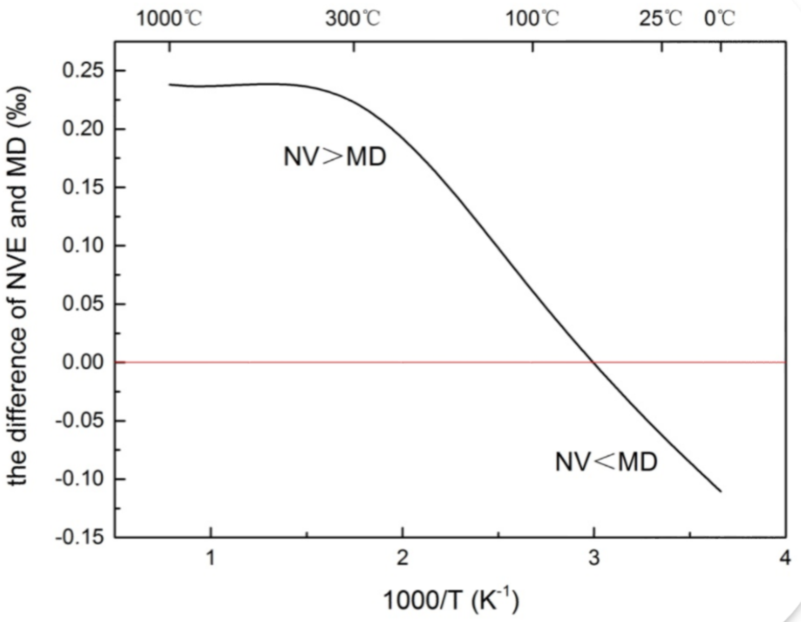
在核电子密度对基组很敏感，因此需要使用尽量大的基组。

Slater基组的计算结果优于Gaussian基组和平面波基组。

Fang and Liu （in preparation）

核体积效应对分馏结果的影响—情况①

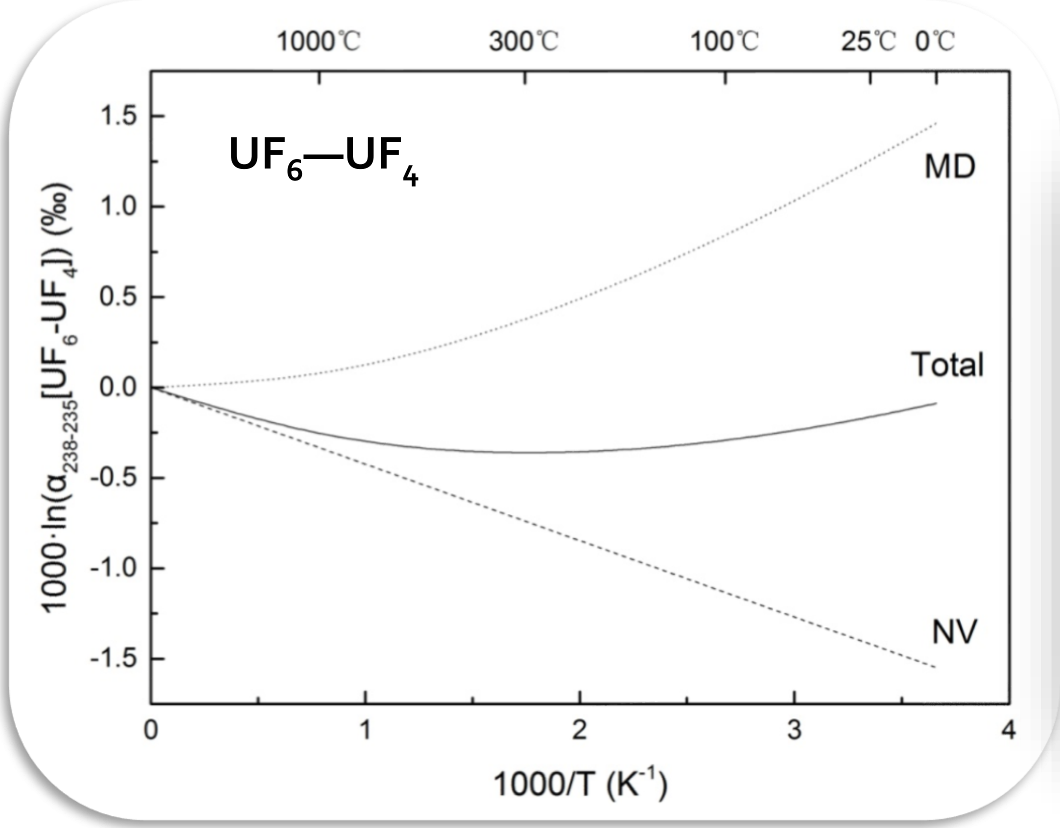




核体积效应分馏方向与质量依赖分馏方向相同，增大总分馏

随温度升高，核体积效应的比重会超过质量依赖分馏

核体积效应对分馏结果的影响—情况②

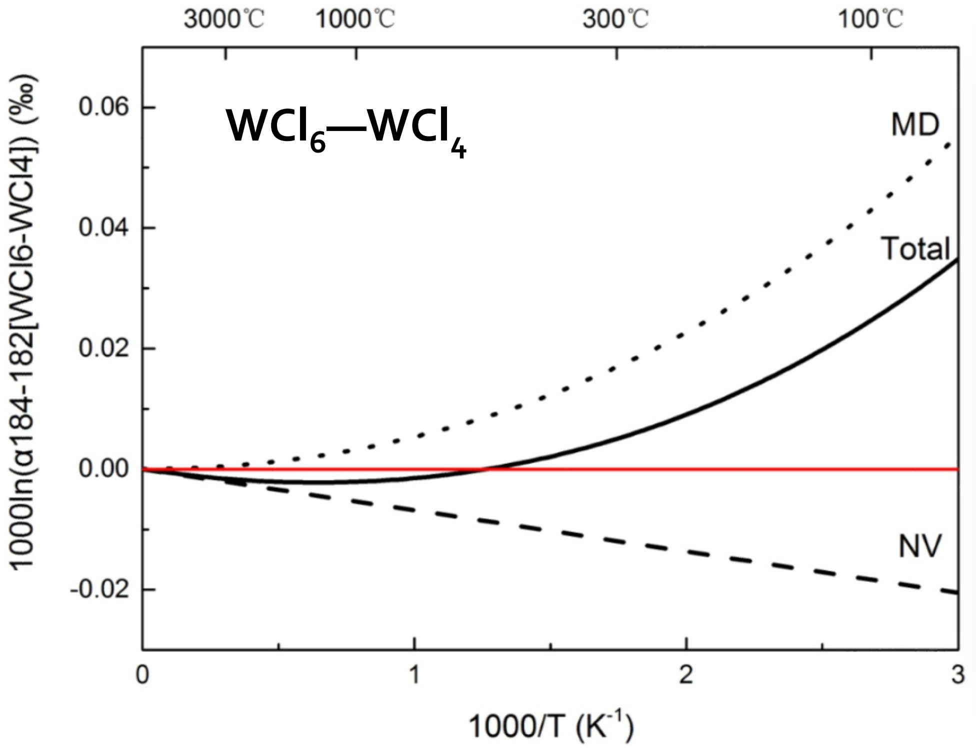


核体积效应分馏方向与质量依赖分馏方向相反，（高价态富集轻同位素）

不同温度下，核体积效应分馏比重都比质量依赖分馏大，总分馏方向与核体积效应保持一致

Fang and Liu （in preparation）

核体积效应对分馏结果的影响—情况③



核体积效应分馏方向与质量依赖分馏方向相反，（高价态富集轻同位素）

温度低时，质量依赖分馏为主
温度高时，核体积效应为主
约400℃时，总分馏由正变负

Fang and Liu （in preparation）

核体积效应对分馏结果的影响

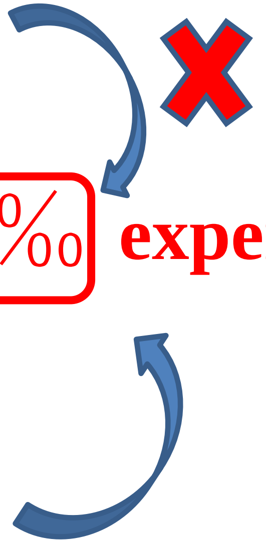
作用

01 核体积效应可以增加分馏程度

02 核体积效应可以改变分馏方向

03 在高温条件下，核体积效应主导分馏方向

$\Delta^{238/235}U_{MD}(UO_2^{2+}{}_{(aq)}-U^{4+}{}_{(aq)}) = \boxed{0.94‰}$ **MD**



$\Delta^{238/235}U_{exp}(UO_2^{2+}{}_{(aq)}-U^{4+}{}_{(aq)}) = \boxed{-1.61‰}$ **experiment**

(Wang et al., 2015)

$\Delta^{238/235}U_{NV+MD}(UO_2^{2+}{}_{(aq)}-U^{4+}{}_{(aq)}) = \boxed{-1.49‰}$ **NV+MD**

$\Delta^{238/235}U_{NV}(UO_2^{2+}{}_{(aq)}-U^{4+}{}_{(aq)}) = \boxed{-2.43‰}$ **NV**

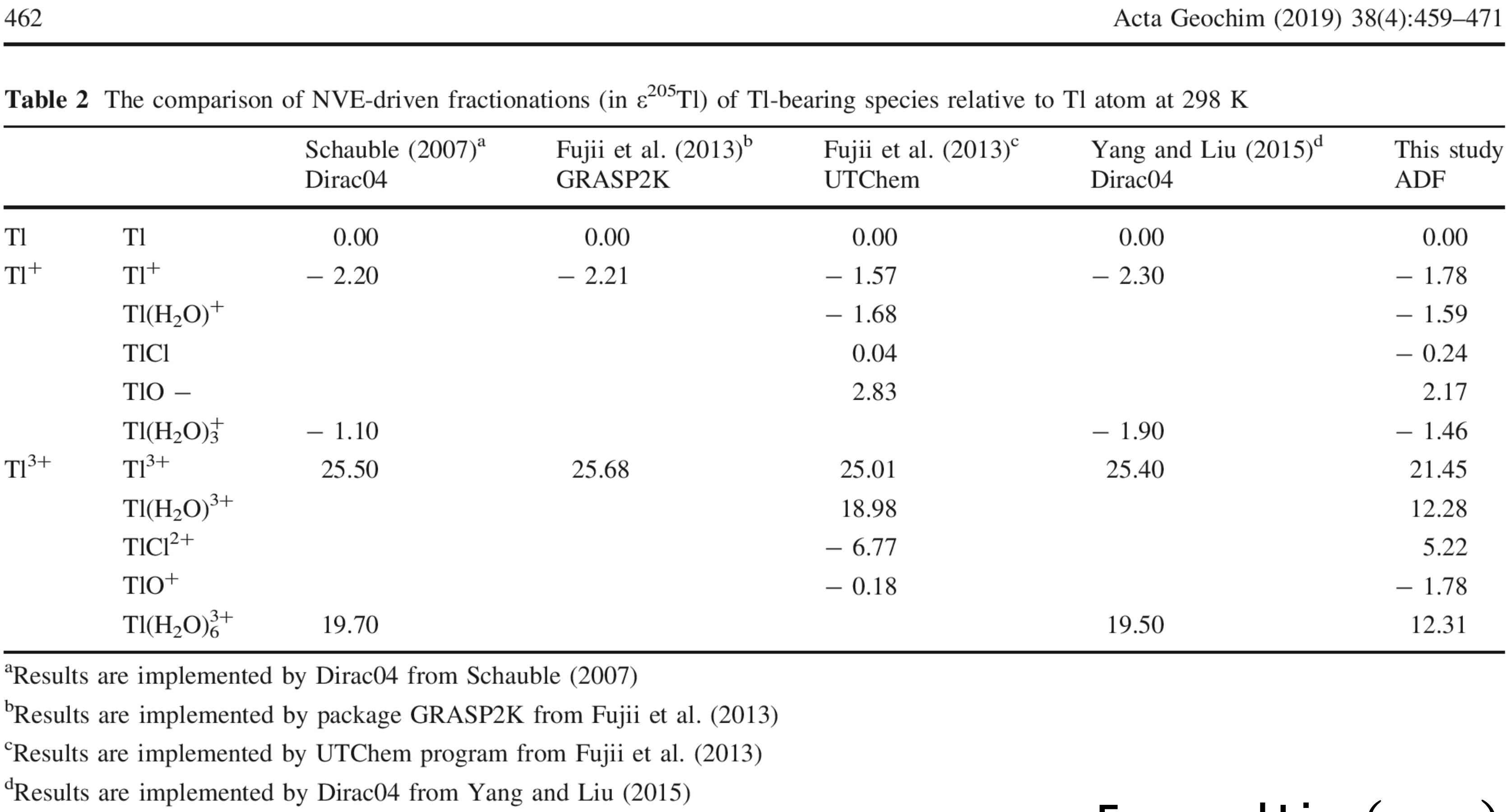


Table 2 The comparison of NVE-driven fractionations (in ε^{205}Tl) of Tl-bearing species relative to Tl atom at 298 K

		Schauble (2007)[a] Dirac04	Fujii et al. (2013)[b] GRASP2K	Fujii et al. (2013)[c] UTChem	Yang and Liu (2015)[d] Dirac04	This study ADF
Tl	Tl	0.00	0.00	0.00	0.00	0.00
$\mathrm{Tl^+}$	$\mathrm{Tl^+}$	− 2.20	− 2.21	− 1.57	− 2.30	− 1.78
	$\mathrm{Tl(H_2O)^+}$			− 1.68		− 1.59
	TlCl			0.04		− 0.24
	TlO −			2.83		2.17
	$\mathrm{Tl(H_2O)_3^+}$	− 1.10			− 1.90	− 1.46
$\mathrm{Tl^{3+}}$	$\mathrm{Tl^{3+}}$	25.50	25.68	25.01	25.40	21.45
	$\mathrm{Tl(H_2O)^{3+}}$			18.98		12.28
	$\mathrm{TlCl^{2+}}$			− 6.77		5.22
	$\mathrm{TlO^+}$			− 0.18		− 1.78
	$\mathrm{Tl(H_2O)_6^{3+}}$	19.70			19.50	12.31

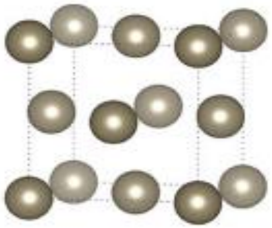
[a] Results are implemented by Dirac04 from Schauble (2007)

[b] Results are implemented by package GRASP2K from Fujii et al. (2013)

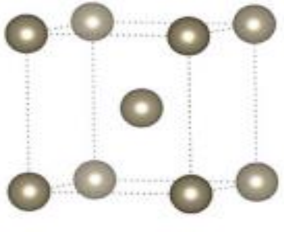
[c] Results are implemented by UTChem program from Fujii et al. (2013)

[d] Results are implemented by Dirac04 from Yang and Liu (2015)

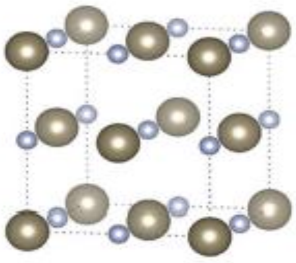
Fang and Liu（2019）



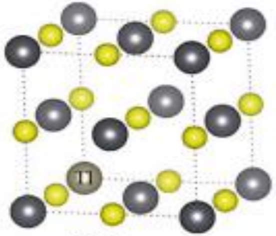
Tl (Fm3m)



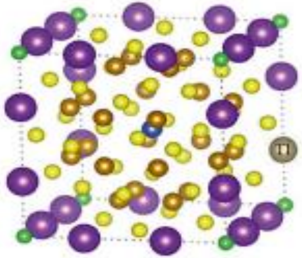
Tl (Im3m)



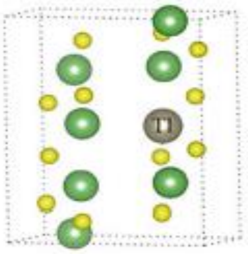
TlF (Im3m)



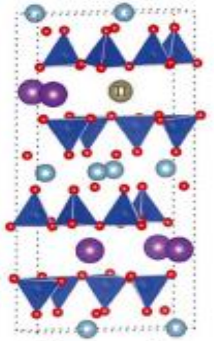
Galena



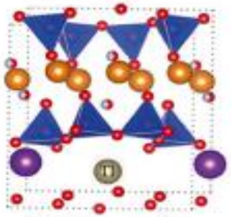
Djerfisherite



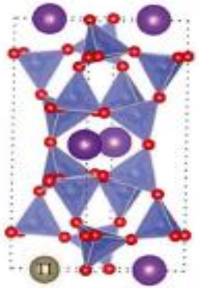
Orpiment



Muscovite



Phlogopite



Feldspar

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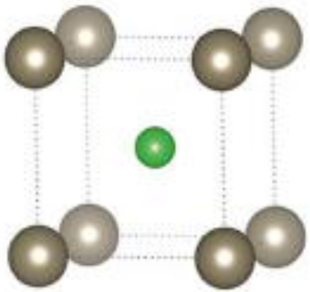
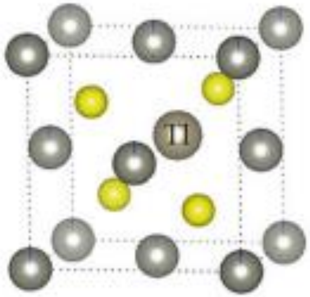
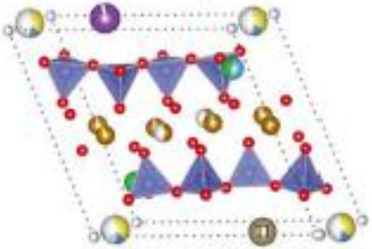


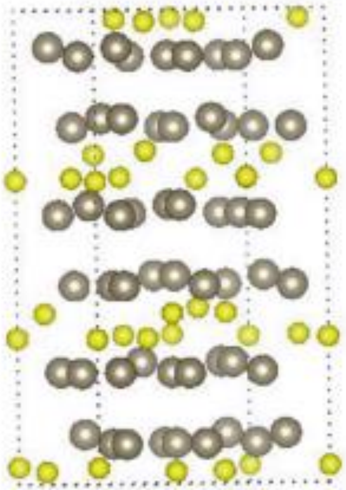
TlCl (Fm3m)



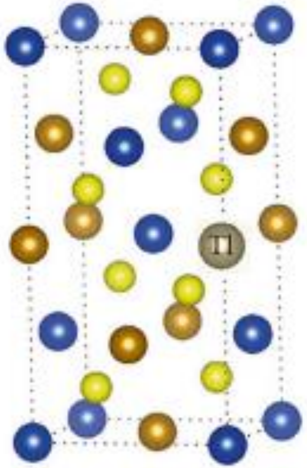
Sphalerite



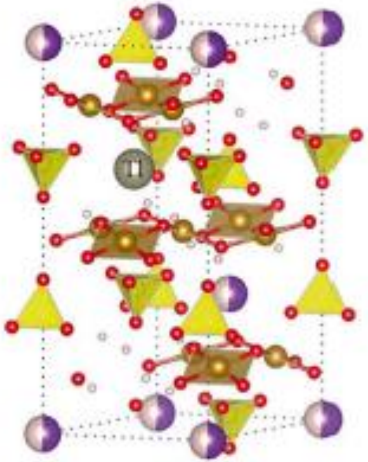
Astrophyllite



Tl_2S (R3)



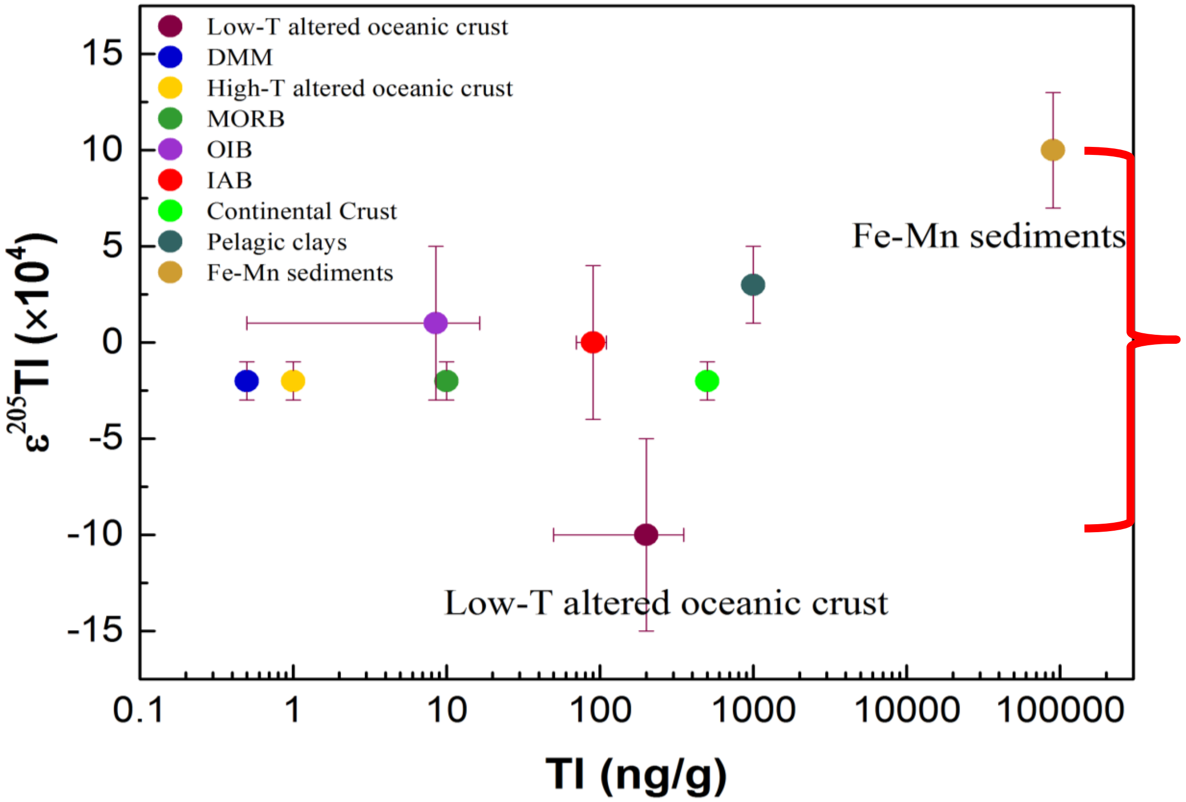
Chalcopyrite



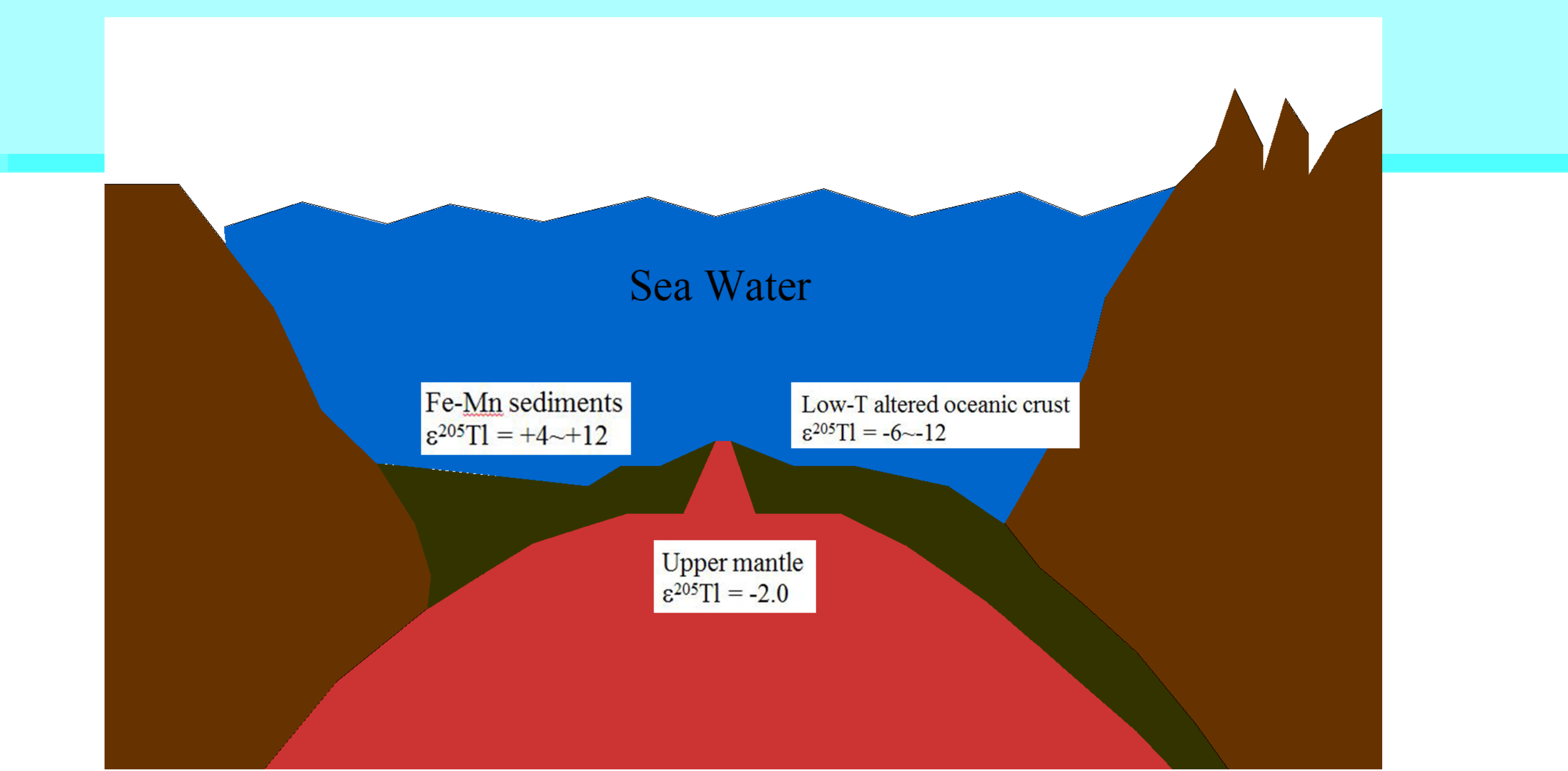
Jarosite

Fang and Liu （2019）

Tl isotope compositions of reservoirs of Earth



~25
ε^{205}Tl



Sea Water

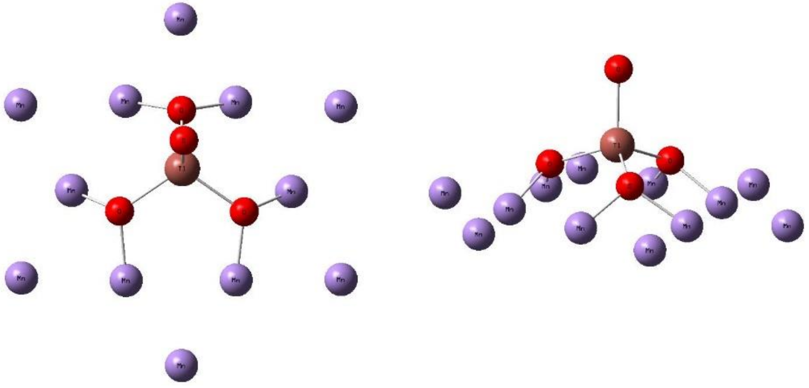
Fe-Mn sediments
$\varepsilon^{205}Tl = +4 \sim +12$

Low-T altered oceanic crust
$\varepsilon^{205}Tl = -6 \sim -12$

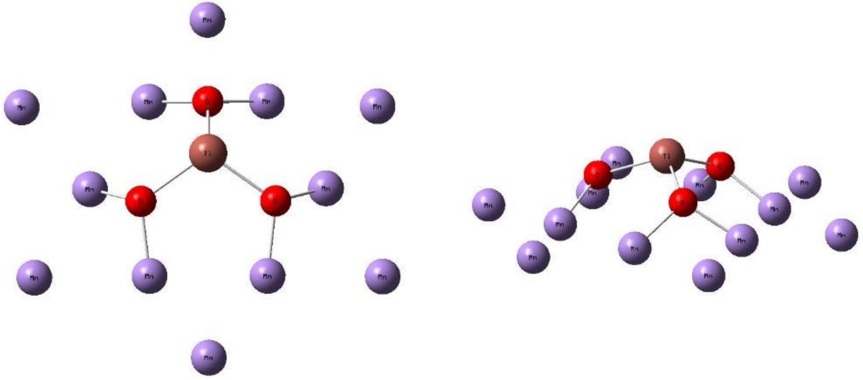
Upper mantle
$\varepsilon^{205}Tl = -2.0$

$$\mathbf{MnO_2(s) + Tl^{+}(aq) + 4H^{+}(aq) \Leftrightarrow Tl^{3+}(aq) + Mn^{2+}(aq) + 2H_2O}$$

Fang and Liu (2019)



Tl_HxBir_pH8_2h



Tl_HxBir_pH8_336h

	0℃	25℃	100℃
Tl_HxBir_pH8_2h(aq) vs. Tl^+(aq)	**10.45**	**9.57**	**7.65**
Tl_HxBir_pH8_2h(aq) vs. TlCl(aq)	**9.97**	**9.13**	**7.30**
Tl_HxBir_pH8_336h(aq) vs. Tl^+(aq)	**8.39**	**7.69**	**6.14**
Tl_HxBir_pH8_336h(aq vs. TlCl(aq)	**7.91**	**7.25**	**5.79**

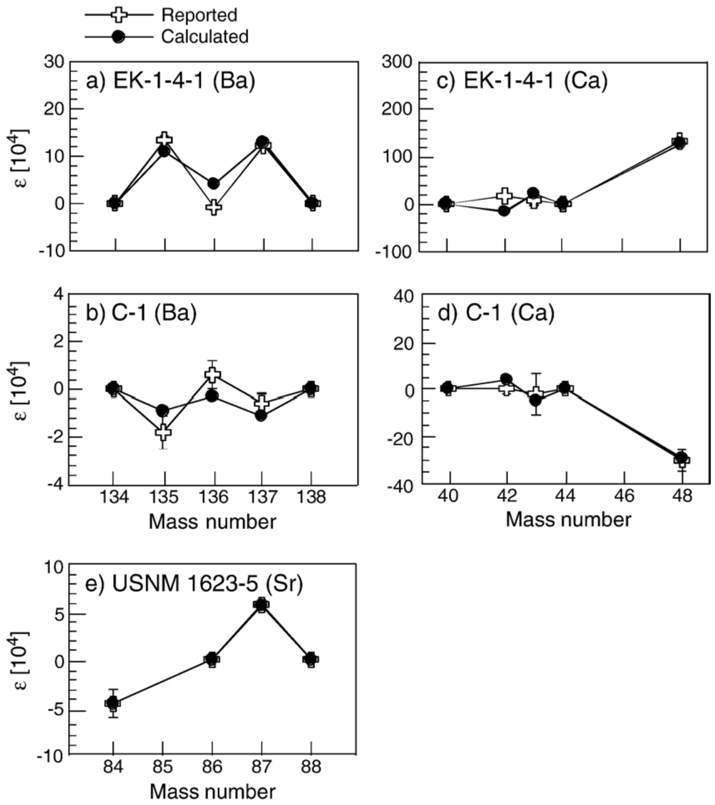
对同位素异常研究方面的影响

真正的首次研究： 2006年 Fujii

$$ln\alpha = \delta\langle r^2\rangle_{m,m'} \times a + \frac{\delta m}{mm'} \times b$$

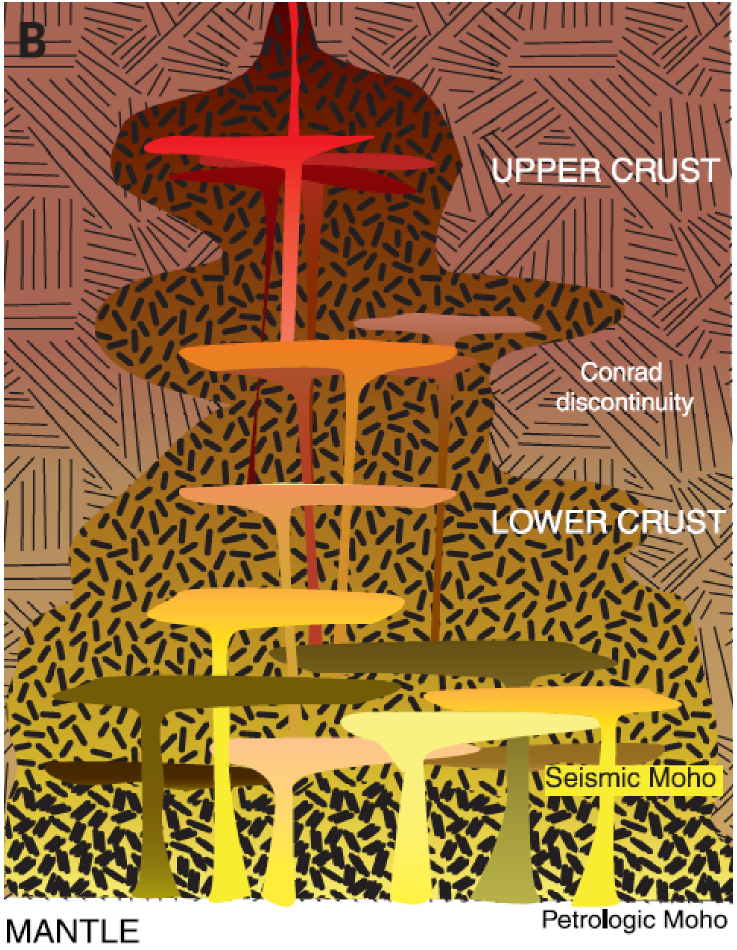
$$\varepsilon_{m_i} = \left(\delta\langle r^2\rangle_{m_1,m_i} - \frac{m_2(m_i-m_1)}{m_i(m_2-m_1)}\delta\langle r^2\rangle_{m_1,m_2}\right) \times a$$

$$a \propto \frac{1}{T};\ b \propto \frac{1}{T^2}$$

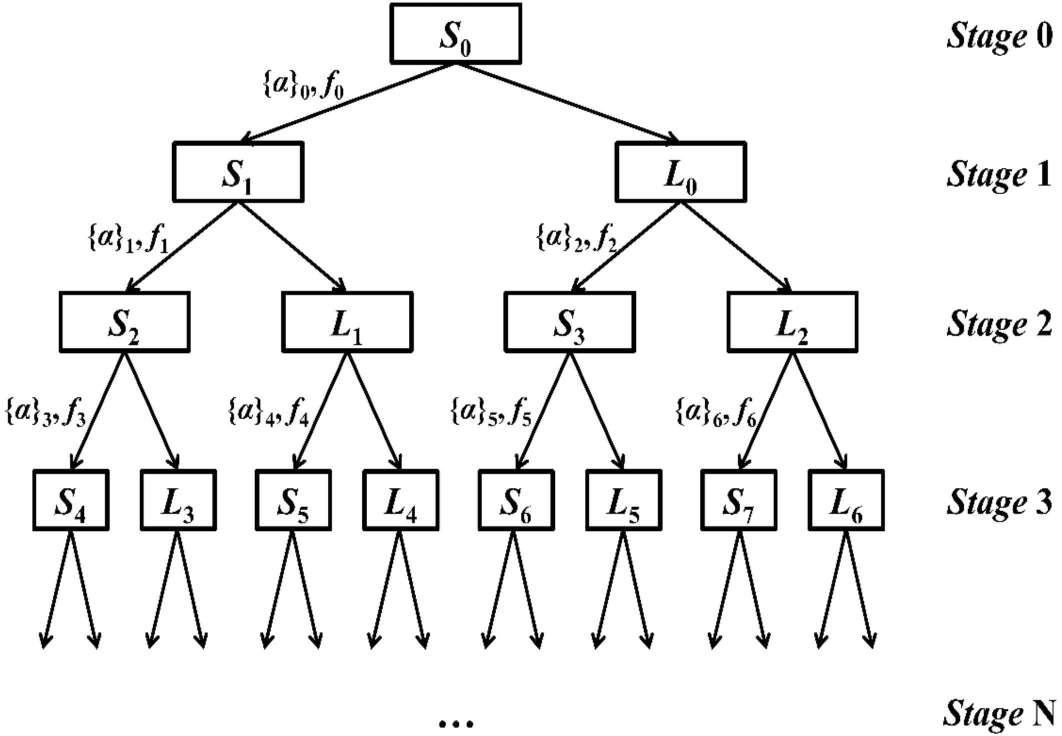


Fujii et al. (2006, EPSL)

“绝命毒师”效应



(Cashman et al., 2017, Science)



Stage 0: S_0

$\{\alpha\}_0, f_0$

Stage 1: S_1, L_0

$\{\alpha\}_1, f_1$ $\{\alpha\}_2, f_2$

Stage 2: S_2, L_1, S_3, L_2

$\{\alpha\}_3, f_3$ $\{\alpha\}_4, f_4$ $\{\alpha\}_5, f_5$ $\{\alpha\}_6, f_6$

Stage 3: S_4, L_3, S_5, L_4, S_6, L_5, S_7, L_6

…

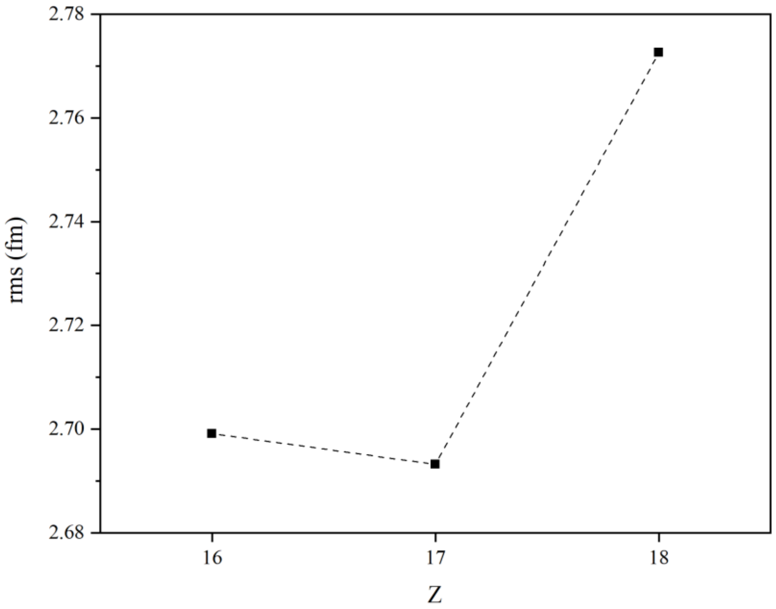
Stage N

How to produce isotope anomalies in mantle by using extremely small isotope fractionations: A process-driven amplification effect?

Yining Zhang [1,2], Yun Liu [1, *]

$$\alpha_{ap}\left(Stage-N\right)=\prod_{i=1}^{N}\alpha_i=\prod_{i=1}^{N}\left(1+\alpha_i-1\right)\approx 1+\sum_{i=1}^{N}\left(\alpha_i-1\right)=1+N\left(\overline{\alpha_i}-1\right)$$

The nuclear-volume effect can be ignored for Oxygen



$$\theta_{DBOC} = \frac{\langle r_{16}^2 \rangle - \langle r_{17}^2 \rangle}{\langle r_{16}^2 \rangle - \langle r_{18}^2 \rangle} = -0.079107$$

Date from Angeli and Marinova (2013)

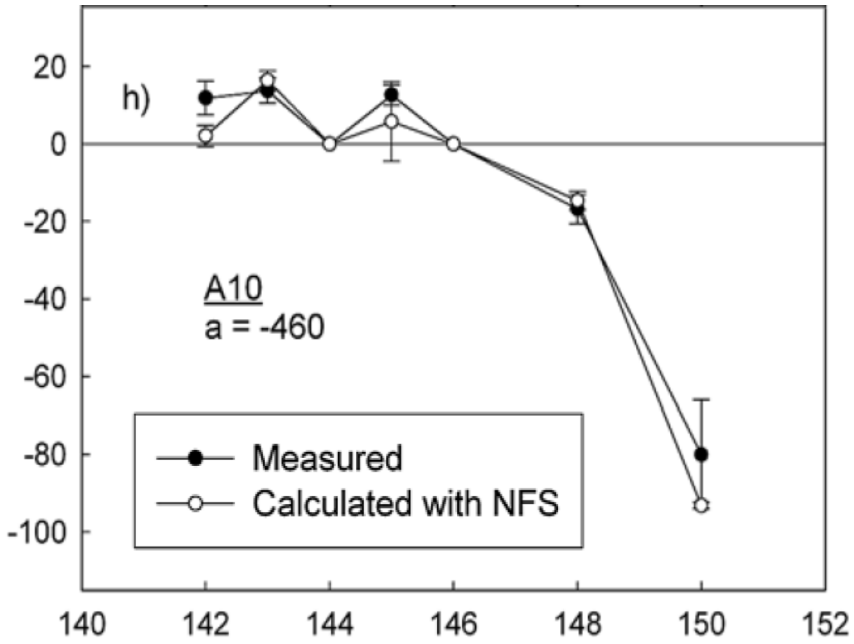
NVE: O_2 - O $^{18}\alpha_{NVE}$ (1500 K) = -1.1 ppm

A 4-component relativistic calculation at

CCSD(T)/aug-cc-pVTZ level by *DIRAC 14.0*

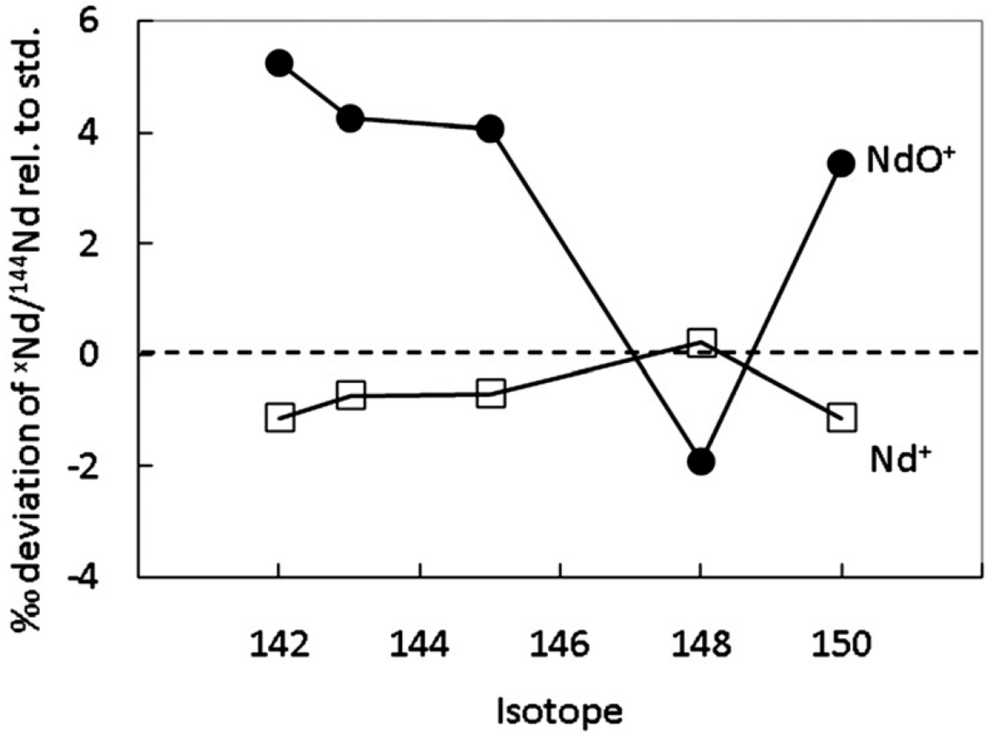
同位素分析中的NVE效应

近年来在采用MC-ICP-MS分析同位素组成的过程中，发现了明显的非质量分馏信号



不同批次的酸淋滤溶液 (Nd^{3+})

Saji et al. (2016, JAAS)



Newman et al. (2009, JAAS)

对定年研究方面的影响

U同位素

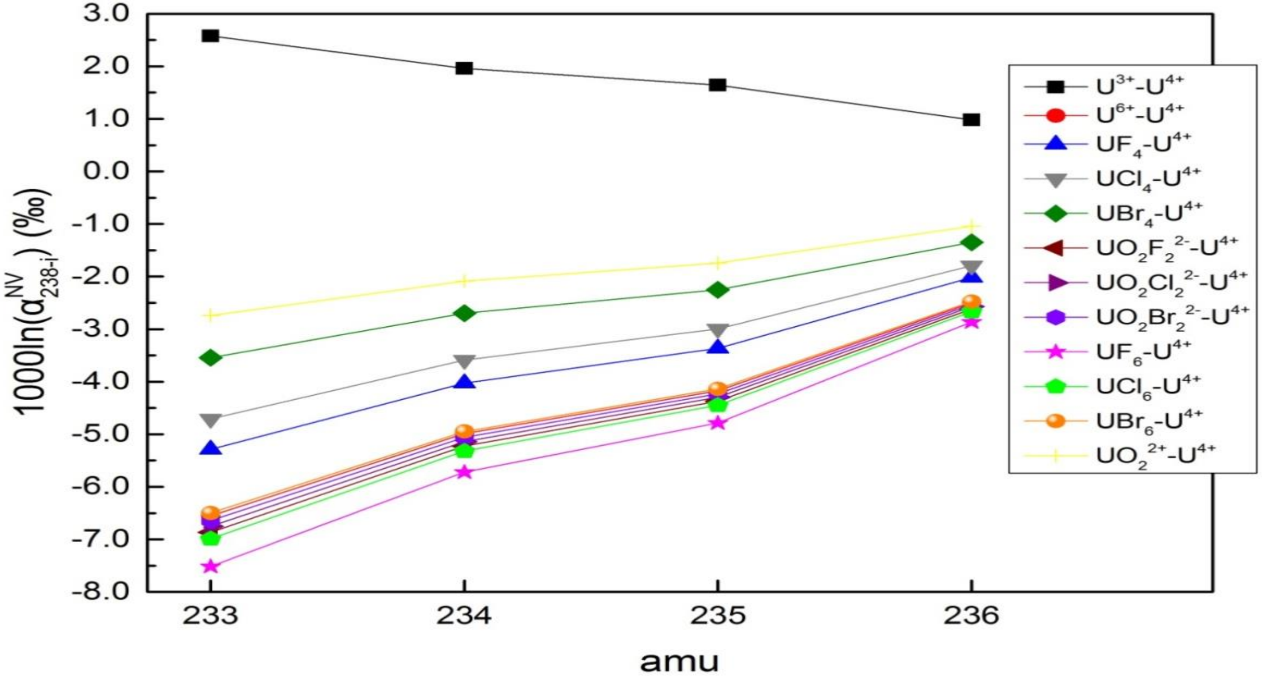
U的地球化学性质：

isotope	NA	half-life	DP
^{233}U	trace	1.592×10^{5}y	^{229}Th
^{234}U	0.005%	2.455×10^{5}y	^{230}Th
^{235}U	0.720%	7.04×10^{8}y	^{231}Th
^{236}U	trace	2.342×10^{7}y	^{232}Th
^{238}U	99.274%	4.468×10^{9}y	α： ^{234}Th β： ^{238}Pu

电子构型：[Rn] $5f^{3}$ $6d^{1}$ $7s^{2}$

氧化态：+**6**, +5, +4, +3, +2, +1(silicate)

U小分子体系核体积效应计算

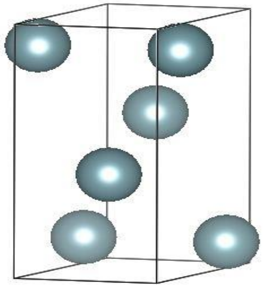


$U^{3+} > U^{4+} > U^{6+}$

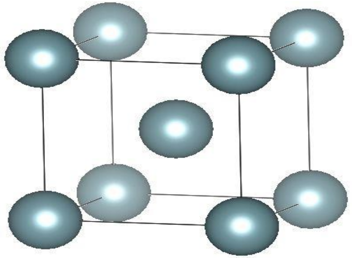
Fig . NVEs-driven $^{238}U-^{i}U$ fractionation factor at 25°C of U-bearing molecules vs. U^{4+}.

Fang and Liu （in preparation）

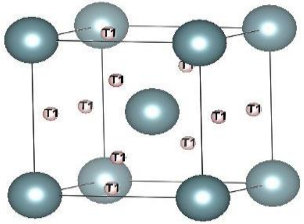
U固体体系



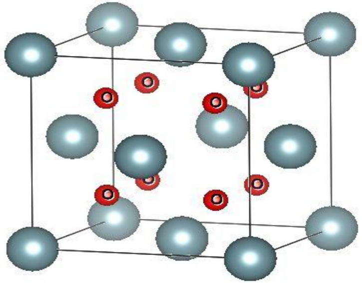
αU



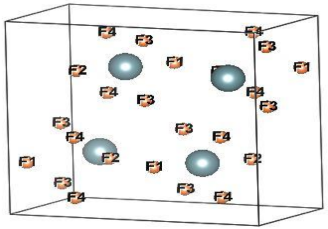
γU



UH_3



UO_2



UF_6

U固体体系核体积效应计算

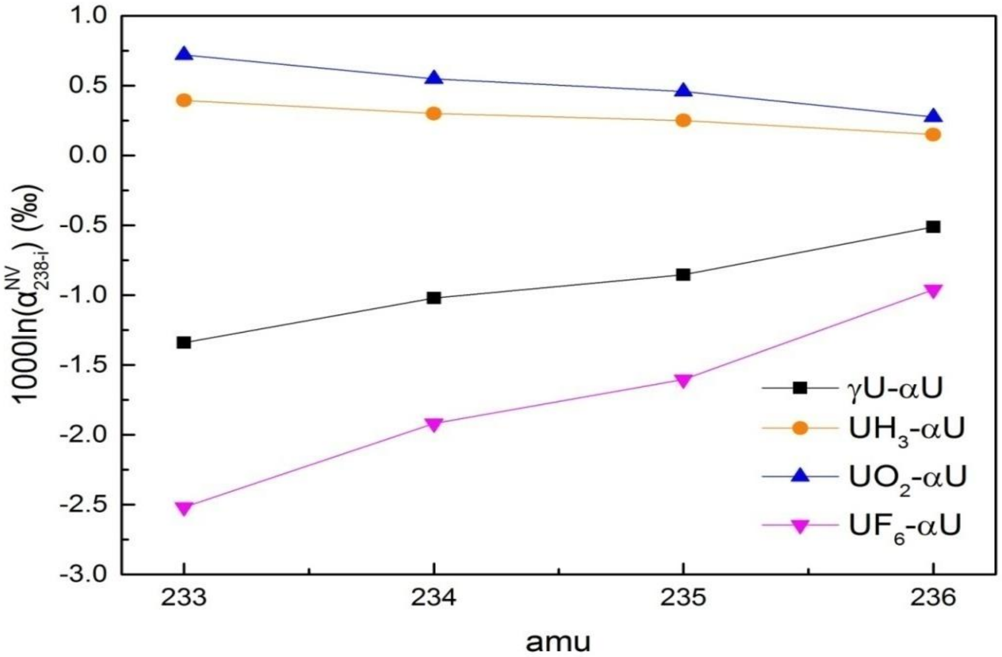


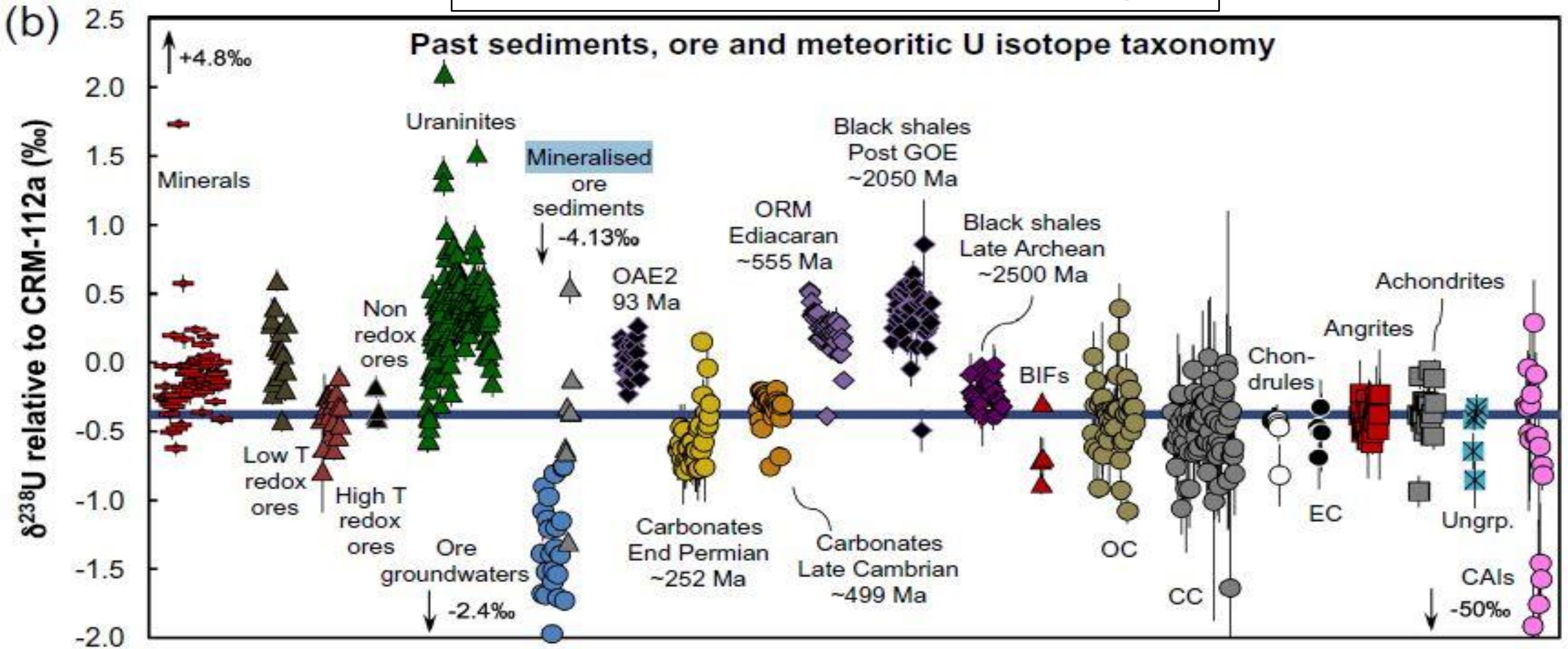
Fig. ^{238}U-^{i}Ufractionation factor at 25°C of U-bearing solids vs. αU

$UO_4 \approx UH_3 > \alpha U > \gamma U > UF_6$

$U^{3+} = U^0$- 2s-1d
$U^{4+} = U^0$- 2s-1d-1f
$U^{6+} = U^0$- 2s-1d-3f

Fang and Liu （in preparation）

U isotope anomaly



(Tissot & Dauphas, 2015)

Correction ages

^{207}Pb-^{206}Pb
:

$$\Delta t = \frac{\boxed{\Delta U'}\left(e^{\lambda_{238}t}-1\right)\left(e^{\lambda_{235}t}-1\right)}{1000\left[\lambda_{238}e^{\lambda_{238}t}-\lambda_{235}e^{\lambda_{235}t}+\left(\lambda_{235}-\lambda_{238}\right)e^{(\lambda_{235}+\lambda_{238})t}\right]}$$

^{206}Pb-^{238}U :

$$\Delta t_8 = 18.467\times 10^{-3}\frac{\boxed{\Delta U'}\left(1-e^{\lambda_{238}t_8}\right)}{1000\lambda_{238}}$$

^{207}Pb-^{235}U :

$$\Delta t_5 = \frac{\boxed{\Delta U'}\left(1-e^{-\lambda_{235}t_5}\right)}{1000\lambda_{235}} + \Delta t_8$$

(Tissot and Dauphas; 2015)

$$\boxed{\Delta U'} = \delta_A - \delta_B \approx \ln \alpha_{A-B} = \ln \beta_A - \ln \beta_B$$

Hf-W二阶段模式年龄

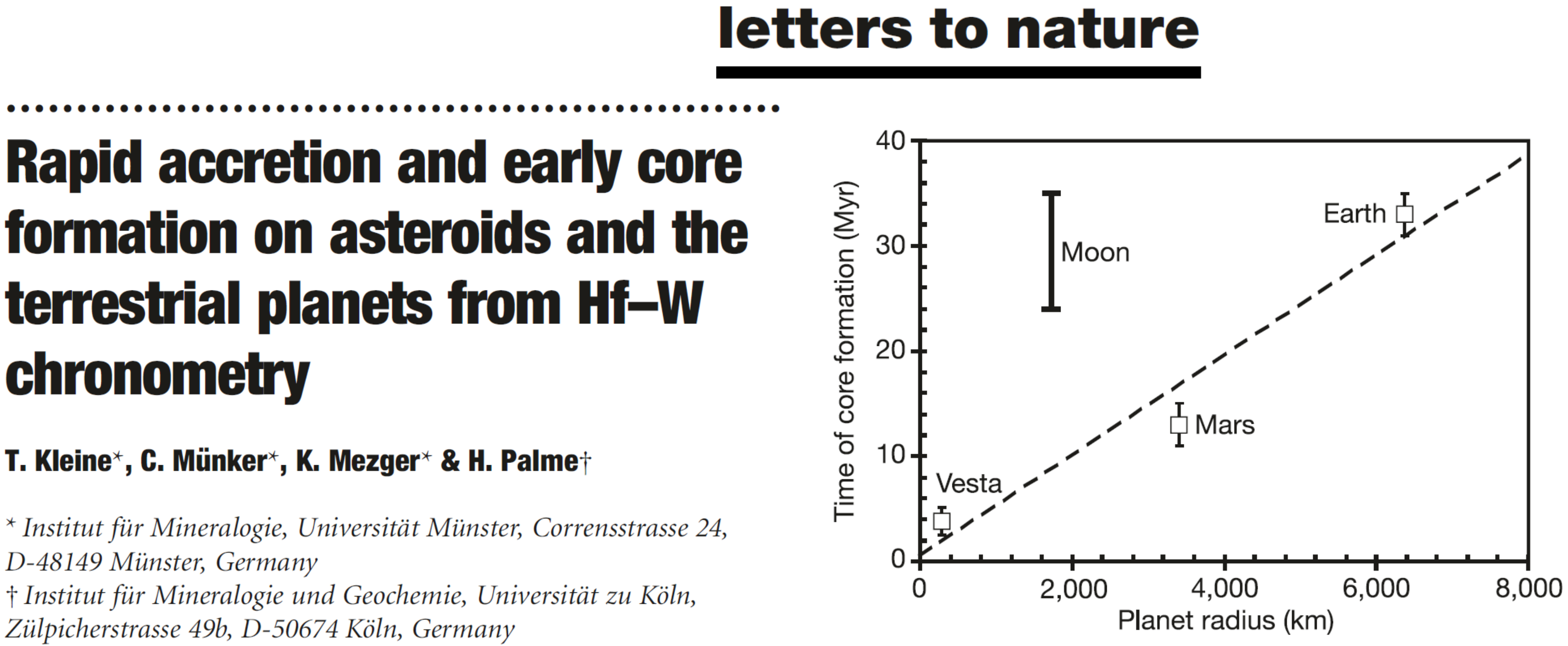
$$\left(\frac{^{182}\mathrm{W}}{^{184}\mathrm{W}}\right)_0 = \left(\frac{^{182}\mathrm{W}}{^{184}\mathrm{W}}\right)_i + \left(\frac{^{180}\mathrm{Hf}}{^{184}\mathrm{W}}\right)_0 \times \left(\frac{^{182}\mathrm{Hf}}{^{180}\mathrm{Hf}}\right)_i$$

$$t_{cf} = \frac{1}{\lambda} \times \ln\left\{\left(\frac{^{182}Hf}{^{180}Hf}\right)_{T_0} \times \frac{\left(\frac{^{180}Hf}{^{184}W}\right)_j - \left(\frac{^{180}Hf}{^{184}W}\right)_{CHUR}}{\left(\frac{^{182}W}{^{184}W}\right)_j - \left(\frac{^{182}W}{^{184}W}\right)_{CHUR}}\right\}$$

$$= \frac{1}{\lambda} \times \ln\left\{\left(\frac{^{182}Hf}{^{180}Hf}\right)_{T_0} \times \frac{(r-1)\left(\frac{^{180}Hf}{^{184}W}\right)_{CHUR}}{\ln \alpha_{j-CHUR}}\right\} \qquad r = \frac{D_{Hf}(M/S)}{D_W(M/S)}$$

applicable only for a single, instantaneous fractionation event.

$$\Delta t_{cf} = \frac{1}{\lambda} \ln\left(\frac{\ln \alpha_{j-CHUR}}{\ln \alpha_{j-CHUR} - \boxed{\ln \alpha_{NV}}}\right)$$



letters to nature

Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf–W chronometry

T. Kleine*, C. Münker*, K. Mezger* & H. Palme†

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Kleine et al. (2002) Nature

化学反应导致的同位素动力学分馏

Kinetic isotope effect （KIE）

只出现在单向反应中

$A+B \rightarrow C+D$ vs. $A+B \leftrightarrow C+D$

- 氧化、还原反应
- 生成气体的反应(气体逃逸)
- 产物极其稳定的反应
- 某些催化反应

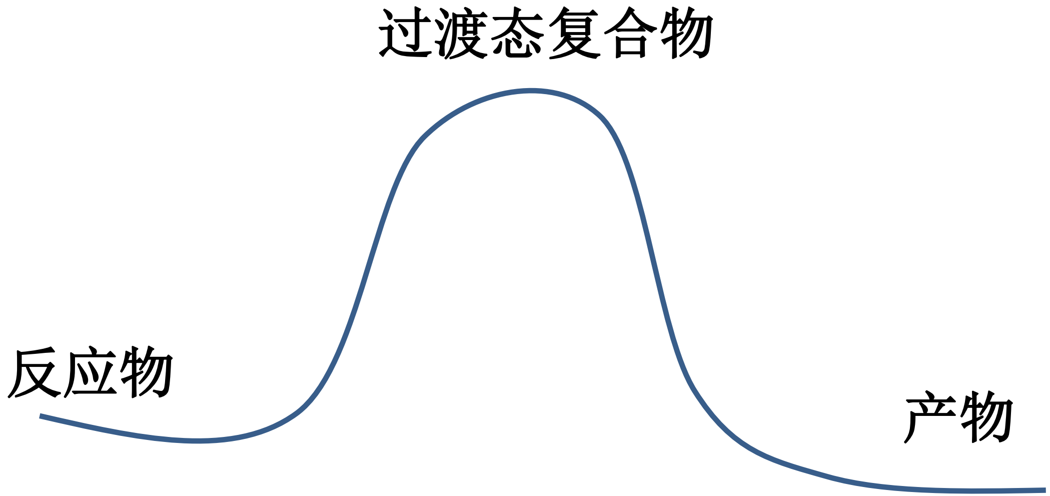
… …

Bigeleisen

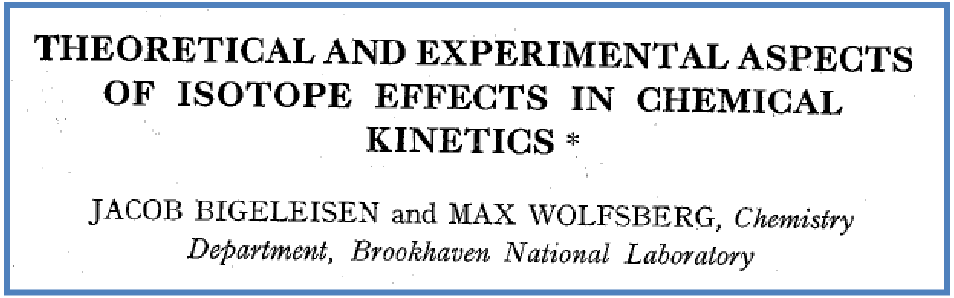
Wolfsberg

化学反应导致的同位素动力学分馏

目前处理化学反应的方式：经久不衰的过渡态理论
H. Eyring（1935）提出
(TST理论)



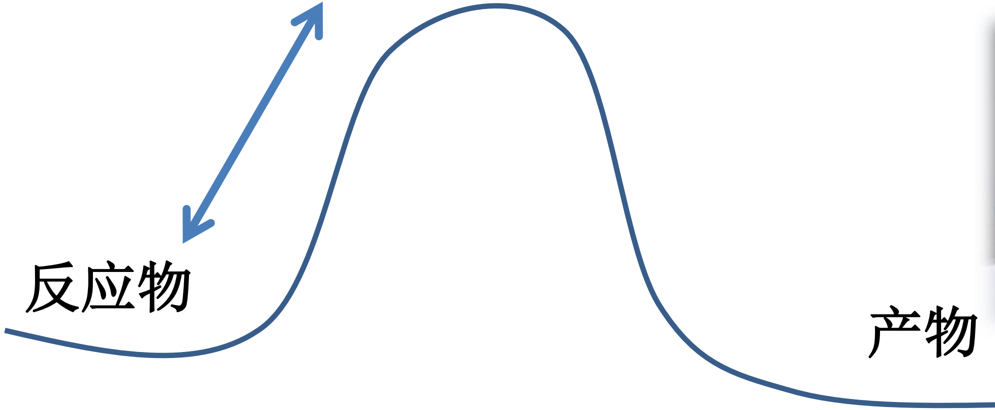
化学反应导致的同位素动力学分馏


THEORETICAL AND EXPERIMENTAL ASPECTS
OF ISOTOPE EFFECTS IN CHEMICAL
KINETICS *

JACOB BIGELEISEN and MAX WOLFSBERG, *Chemistry*
Department, Brookhaven National Laboratory

（1958）


Bigeleisen

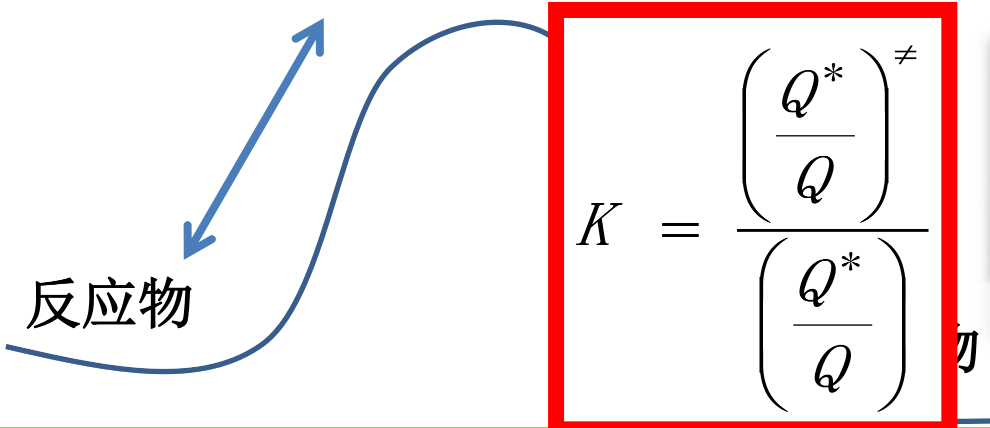



Wolfsberg

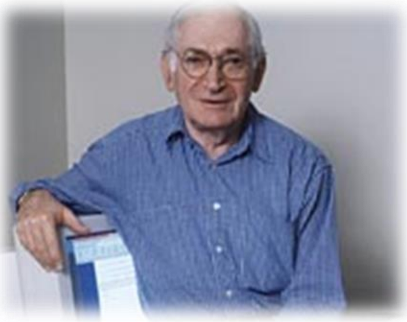
化学反应导致的同位素动力学分馏

化学反应动力学分馏的大小，是过渡态复合物与反应物之间**平衡分馏**的值

Bigeleisen

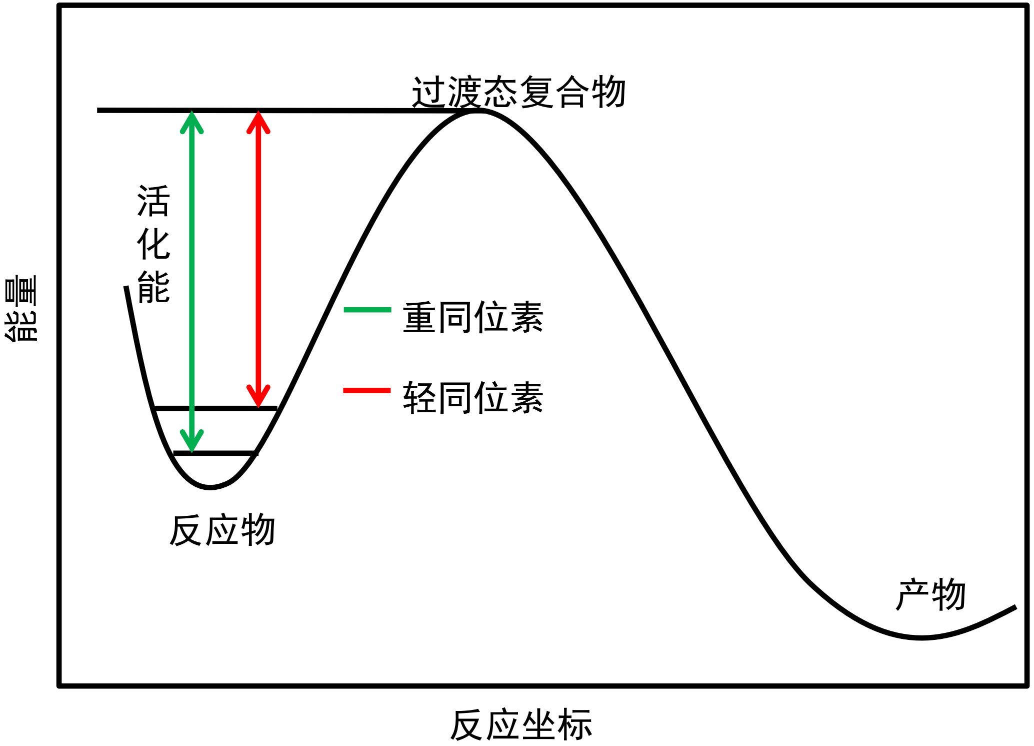


$$K = \frac{\left(\frac{Q^*}{Q}\right)^{\neq}}{\left(\frac{Q^*}{Q}\right)}$$



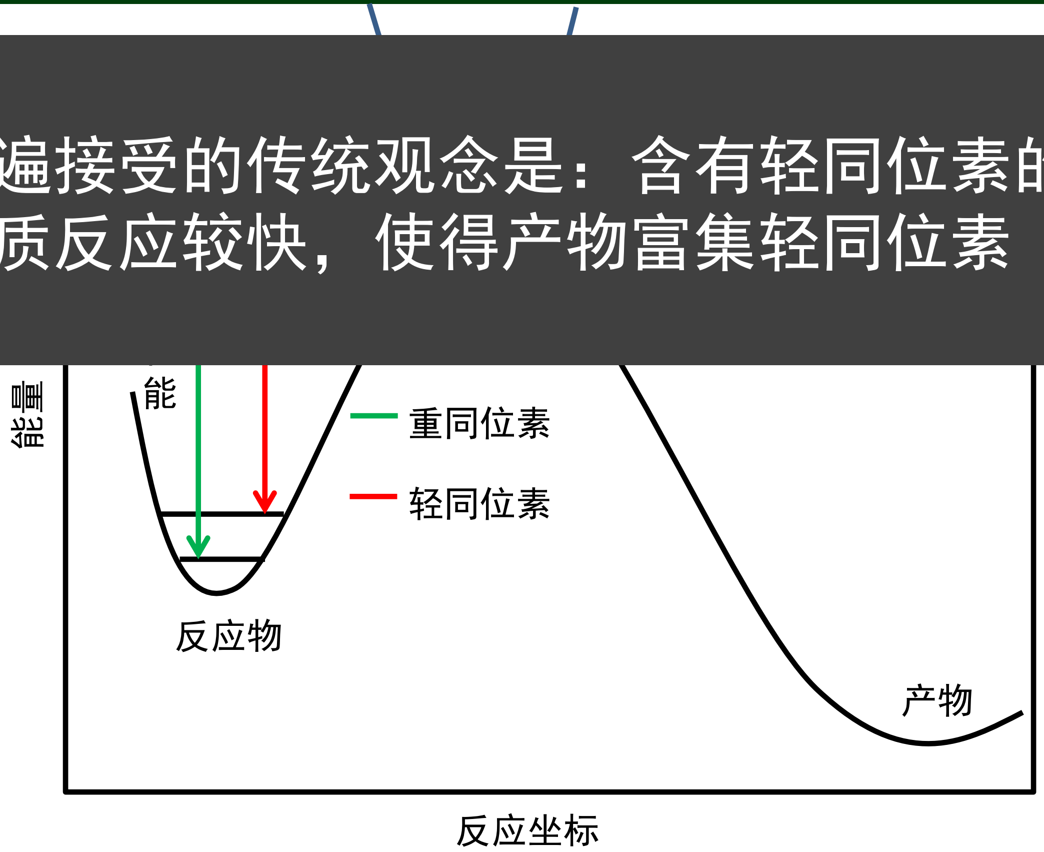
Wolfsberg

化学反应导致的同位素动力学分馏

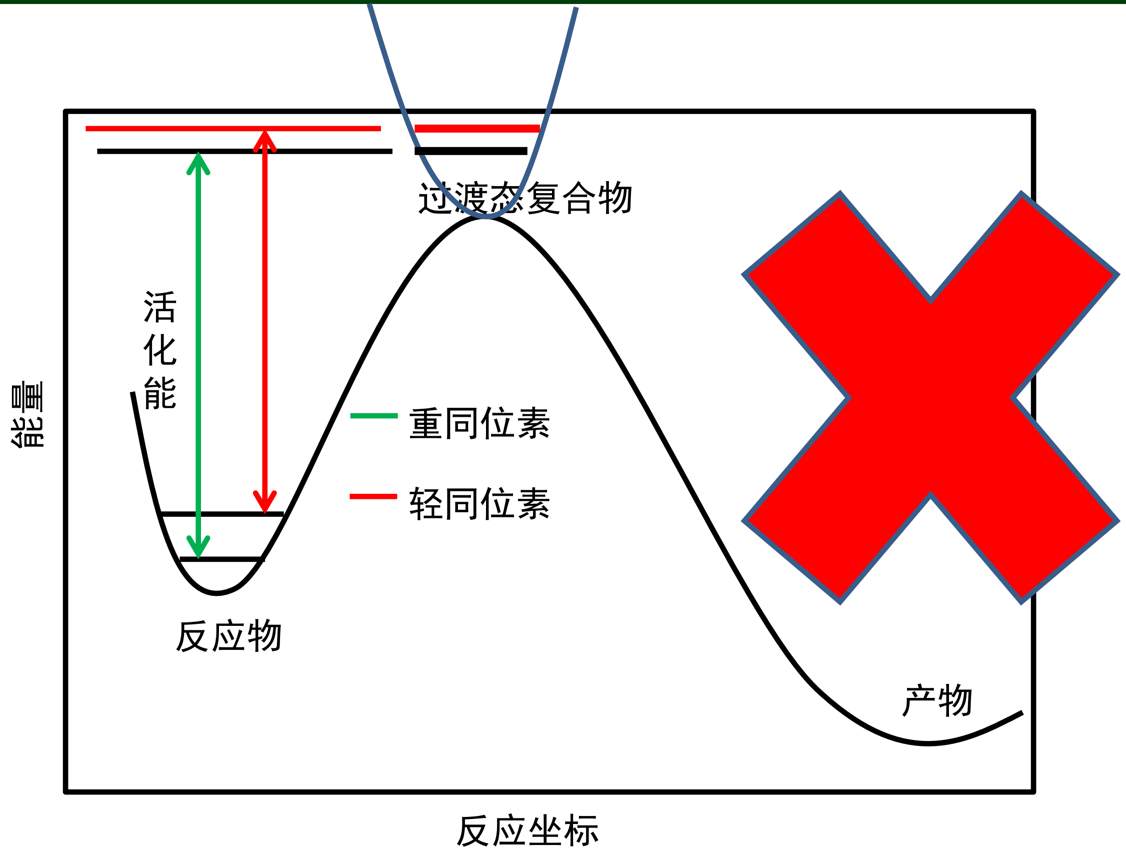


化学反应导致的同位素动力学分馏

普遍接受的传统观念是：含有轻同位素的分子或物质反应较快，使得产物富集轻同位素



化学反应导致的同位素动力学分馏

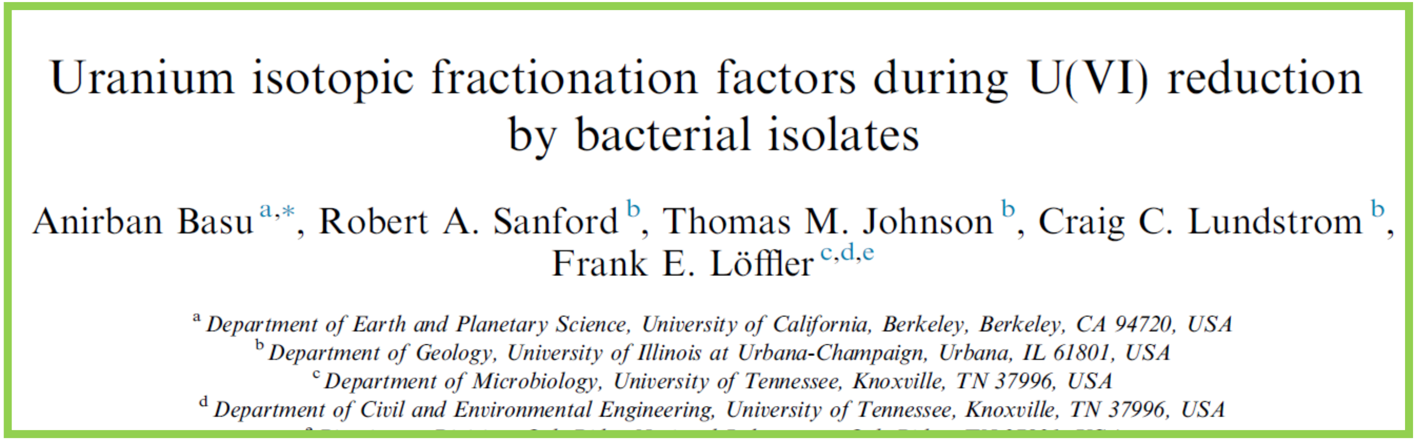


异常的反应动力学分馏效应

Se（VI）还原反应 → 产物富集轻的Se同位素

Cr（VI）还原反应 → 产物富集轻的Cr同位素

U（VI）还原反应 → 产物富集重的U同位素



Uranium isotopic fractionation factors during U(VI) reduction by bacterial isolates

Anirban Basu[a,*], Robert A. Sanford[b], Thomas M. Johnson[b], Craig C. Lundstrom[b], Frank E. Löffler[c,d,e]

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[b] *Department of Geology, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA*
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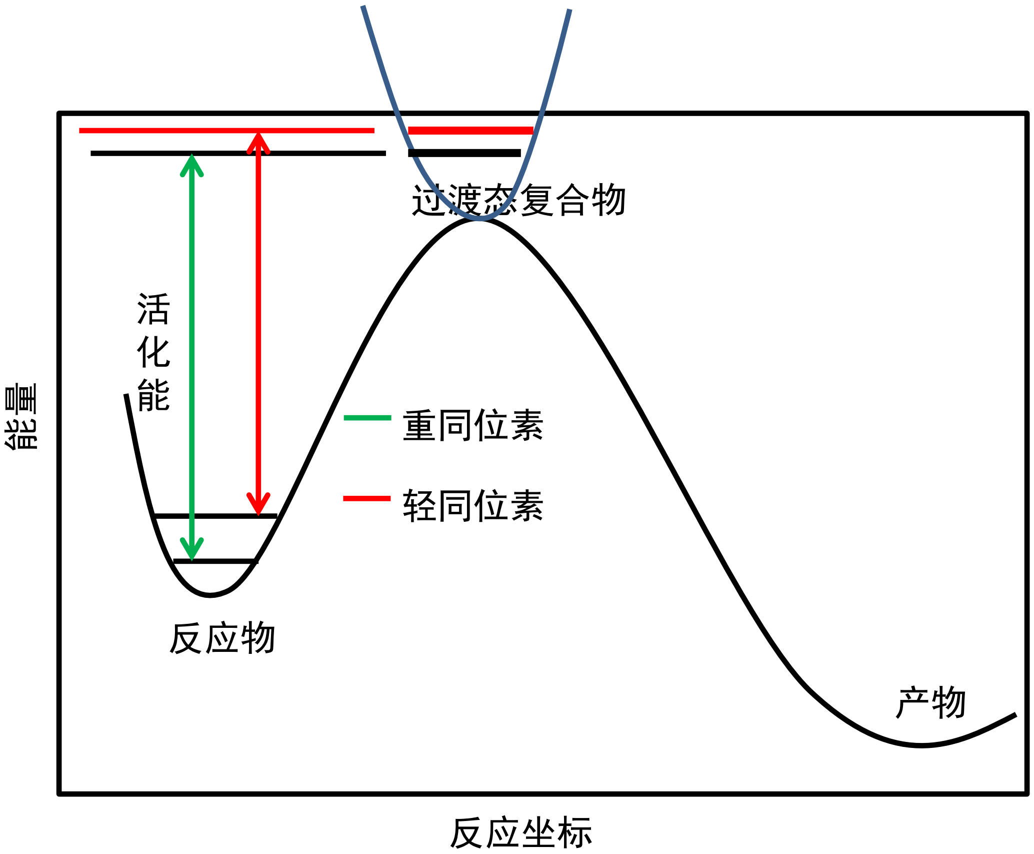
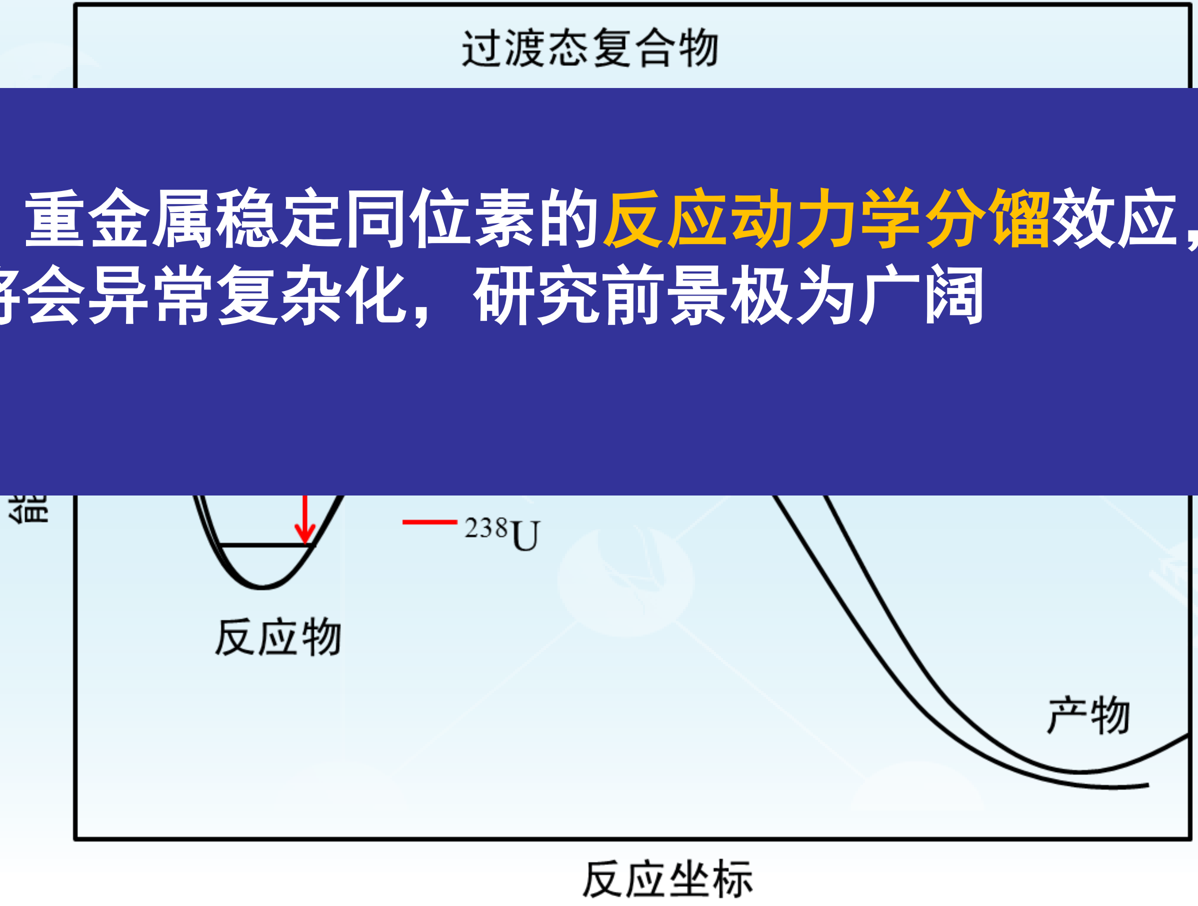
[d] *Department of Civil and Environmental Engineering, University of Tennessee, Knoxville, TN 37996, USA*

(Basu et al., 2014, GCA)

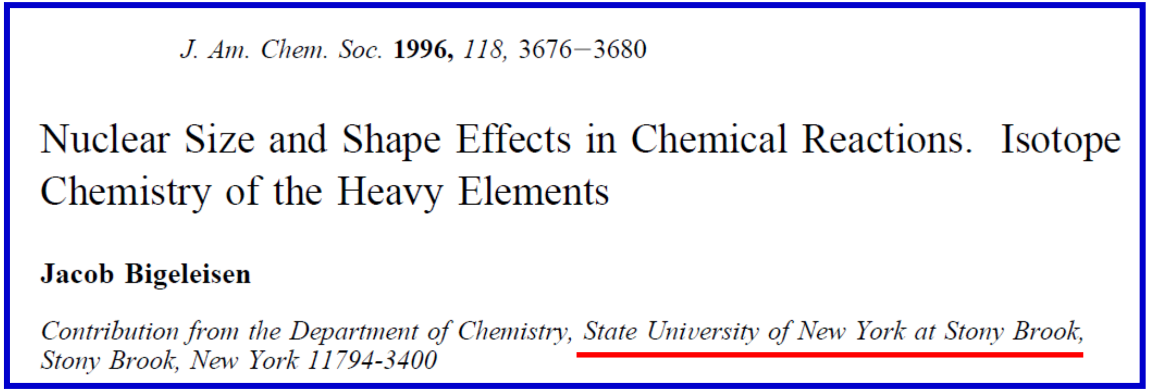

过渡态复合物
活化能
重同位素
轻同位素
反应物
产物
能量
反应坐标

重金属稳定同位素的**反应动力学分馏**效应，将会异常复杂化，研究前景极为广阔



Yang and Liu （2016）

本堂课需要记住的知识点



J. Am. Chem. Soc. **1996,** *118,* 3676–3680

Nuclear Size and Shape Effects in Chemical Reactions. Isotope Chemistry of the Heavy Elements

Jacob Bigeleisen

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400

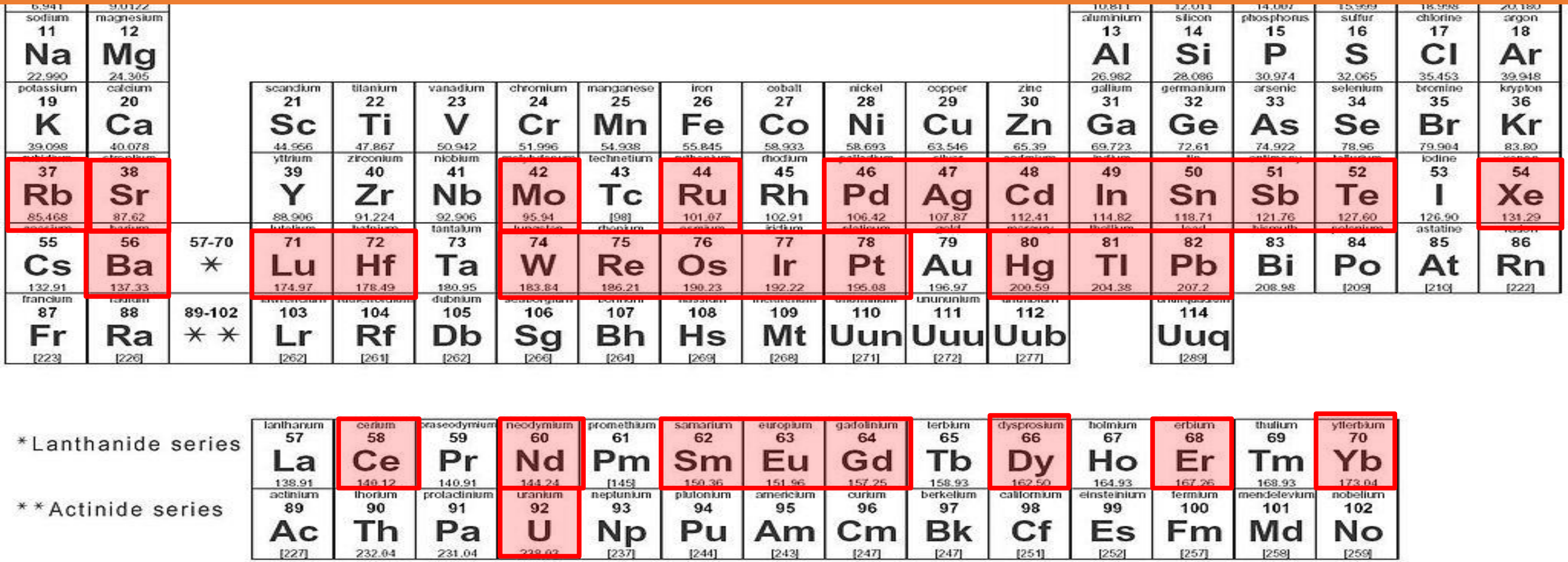
Bigeleisen

$$\ln\alpha=\ln\alpha_0+\ln K_{anh}+\ln K_{BOELE}+\ln K_{hf}+\boxed{\ln K_{fs}}$$

+ 压力效应

核体积效应

具较显著核体积效应的体系



6.941	9.0122												10.811	12.011	14.007	15.999	18.998	20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
37 Rb 85.468	38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	42 Mo 95.94	technetium 43 Tc [98]	44 Ru 101.07	rhodium 45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	iodine 53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-70 *	71 Lu 174.97	72 Hf 178.49	tantalum 73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	astatine 85 At [210]	86 Rn [222]
francium 87 Fr [223]	88 Ra [226]	89-102 * *	103 Lr [262]	104 Rf [261]	dubnium 105 Db [262]	106 Sg [266]	107 Bh [264]	108 Hs [269]	109 Mt [268]	110 Uun [271]	unununium 111 Uuu [272]	112 Uub [277]		114 Uuq [289]				

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
* *Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

谢 谢！