

铀—铅年代学

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Isotopes in Geosciences

1. Stable Isotope Geochemistry

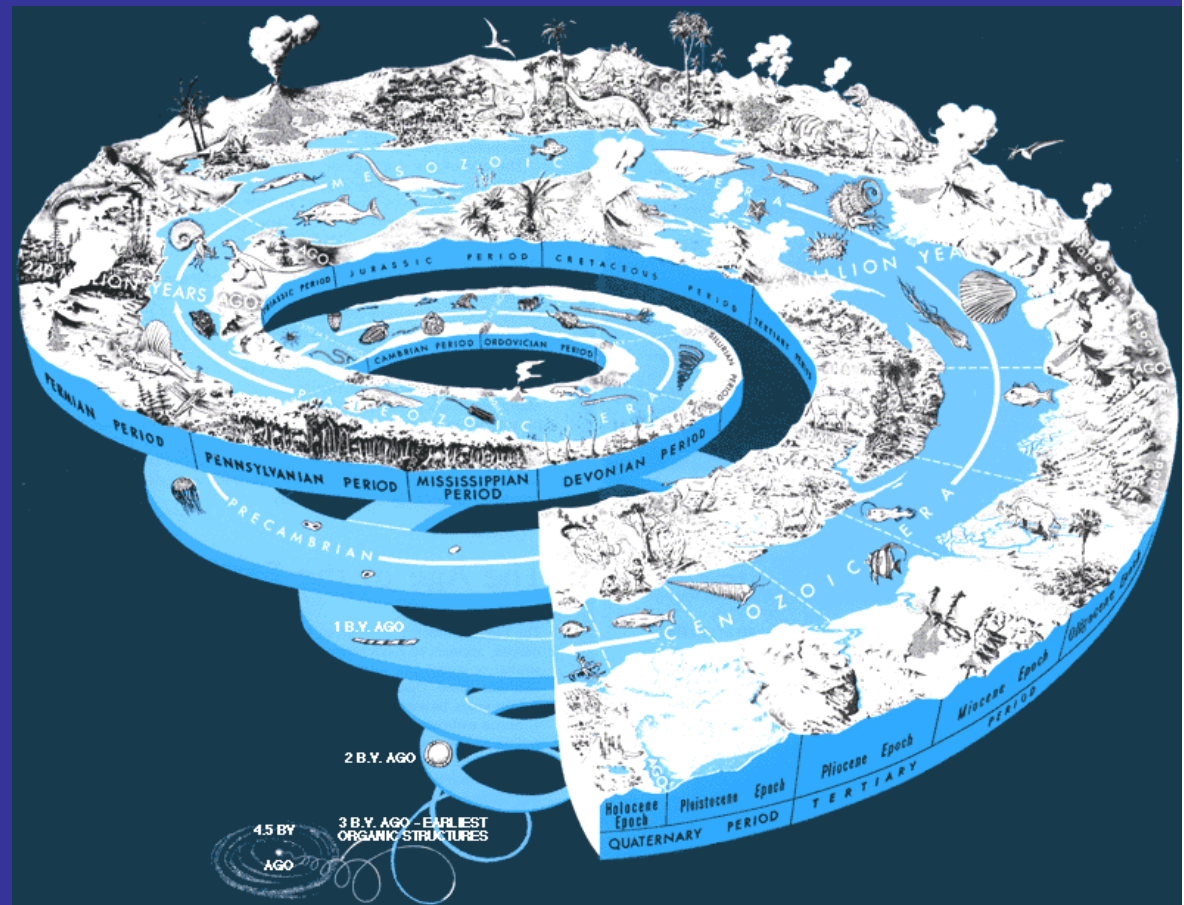
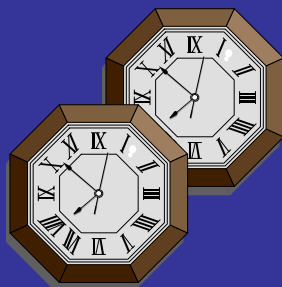
2. Radiogenic Isotope Geochemistry

(1) Geochronology

(2) Isotopic Tracer

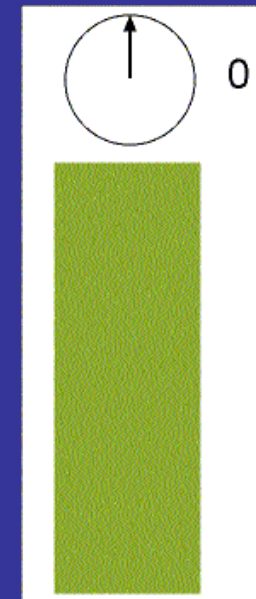
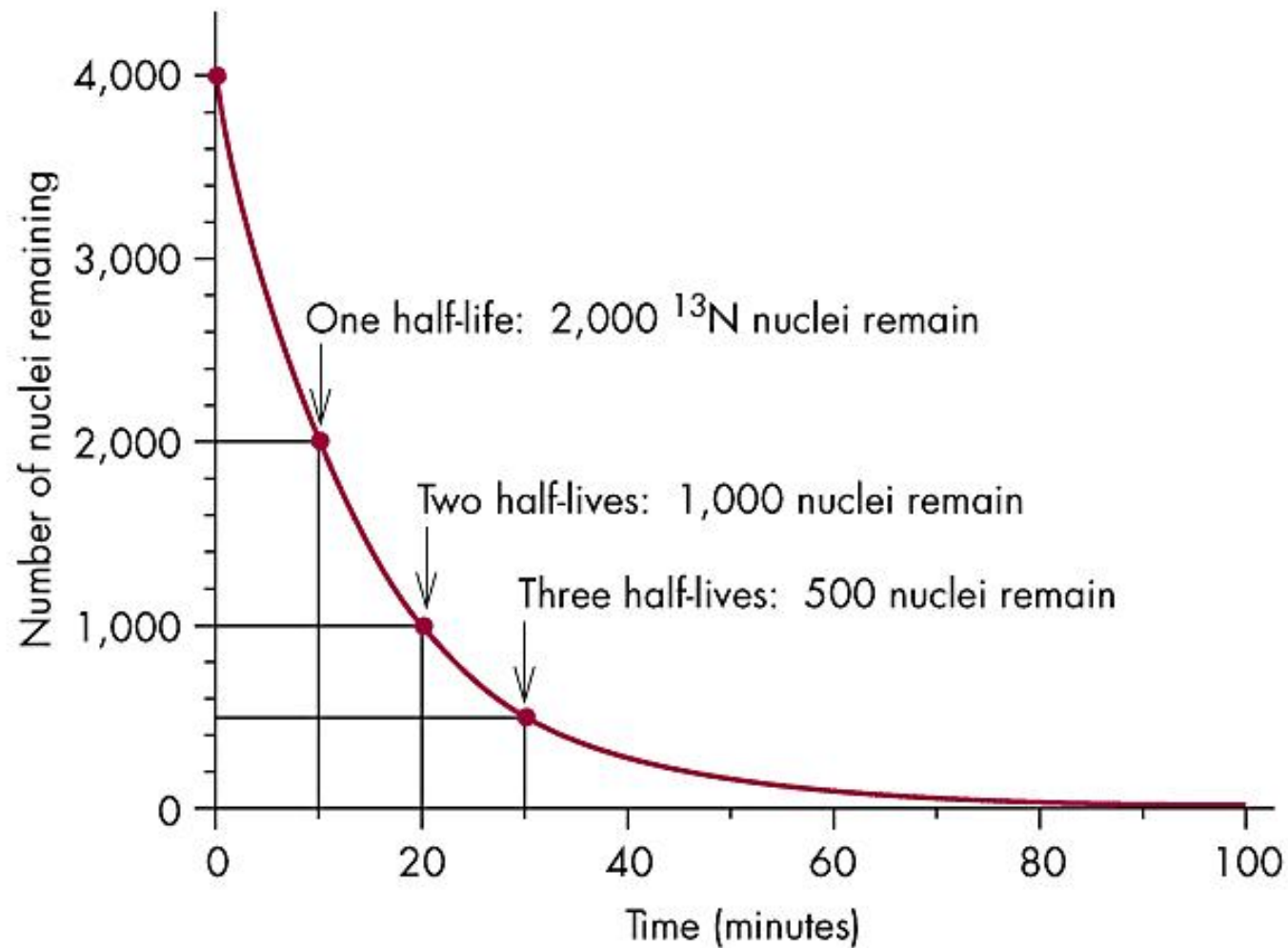
Isotope Geochronology

Radiometric dating -
A time machine
to the past



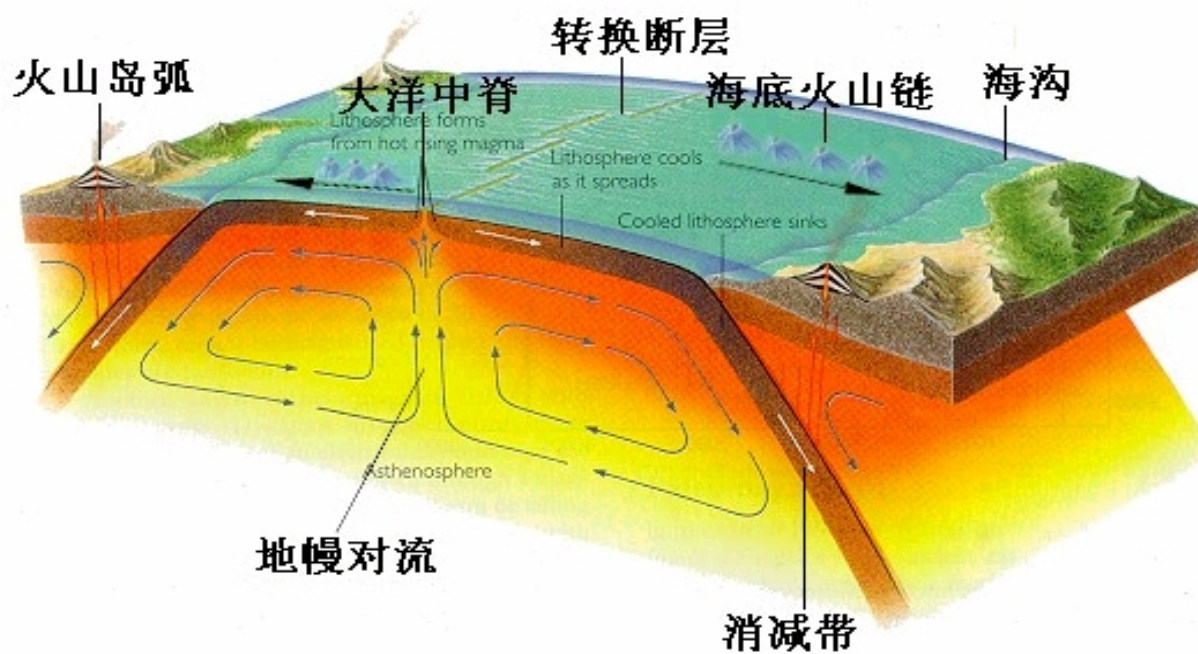
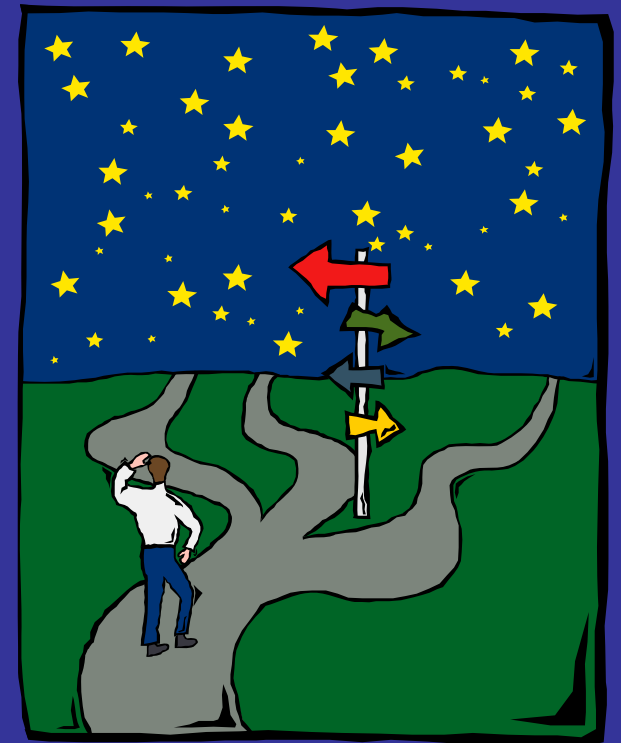
Radioactive decay

half-lives, $T_{1/2}$



Isotopic Tracer

How do we know where the rocks came from?

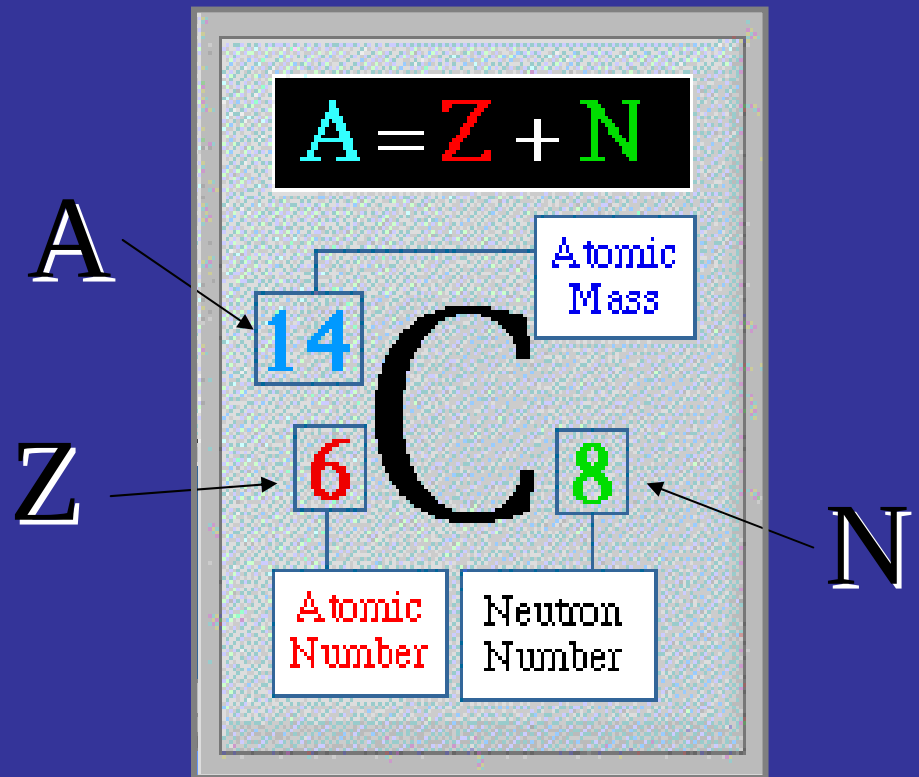


Component of an atom for geochemists' interest

Proton (Z)

Neutron (N)

Electron (E)



Atoms of an element can
have different weight

For instance:

Atom1: Weight (A_1) = $Z + N_1$

Atom2: Weight (A_2) = $Z + N_2$

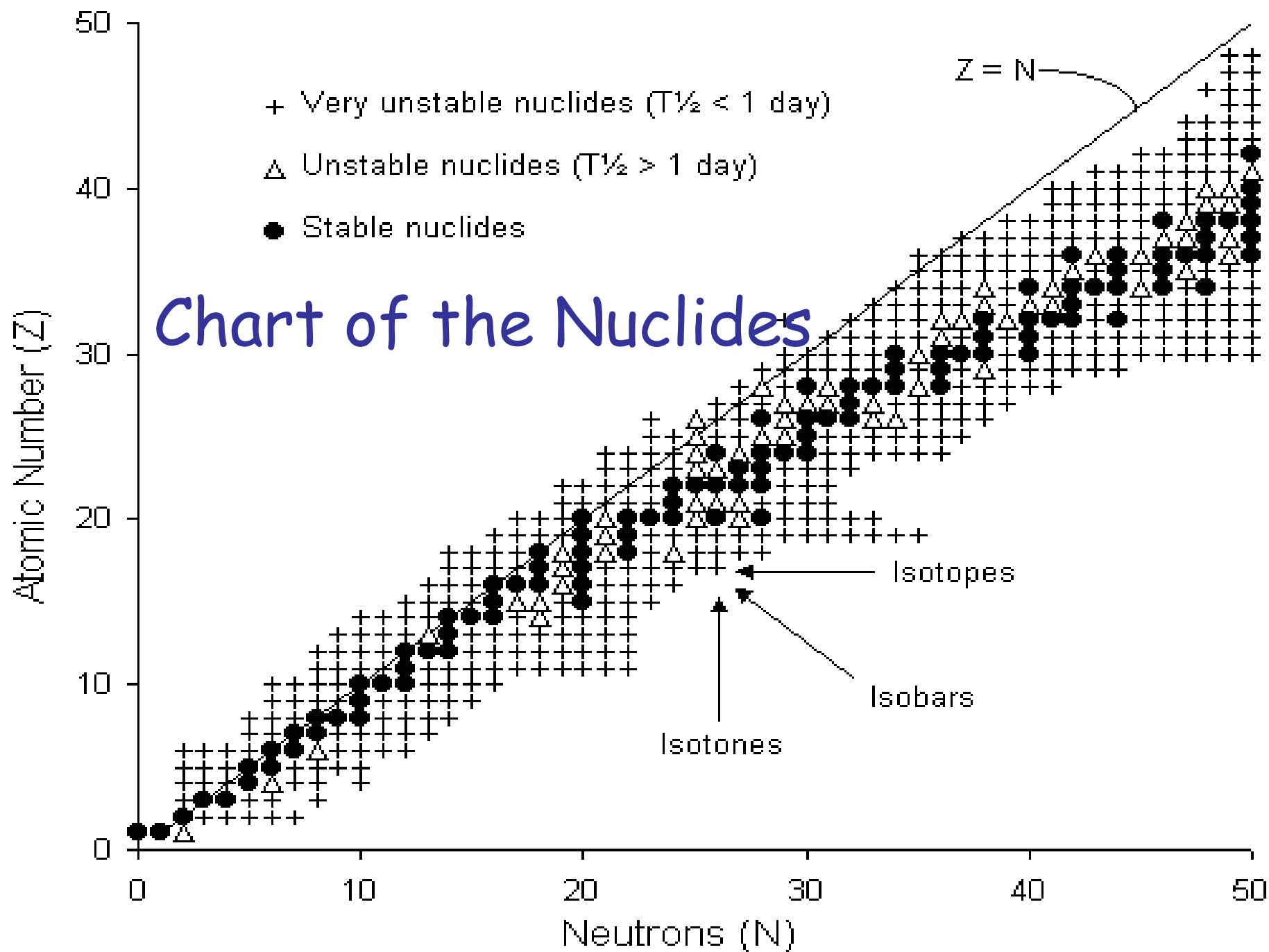
Such atoms are isotopes

Isobar

Different elements have the same weight number (A), but different Z

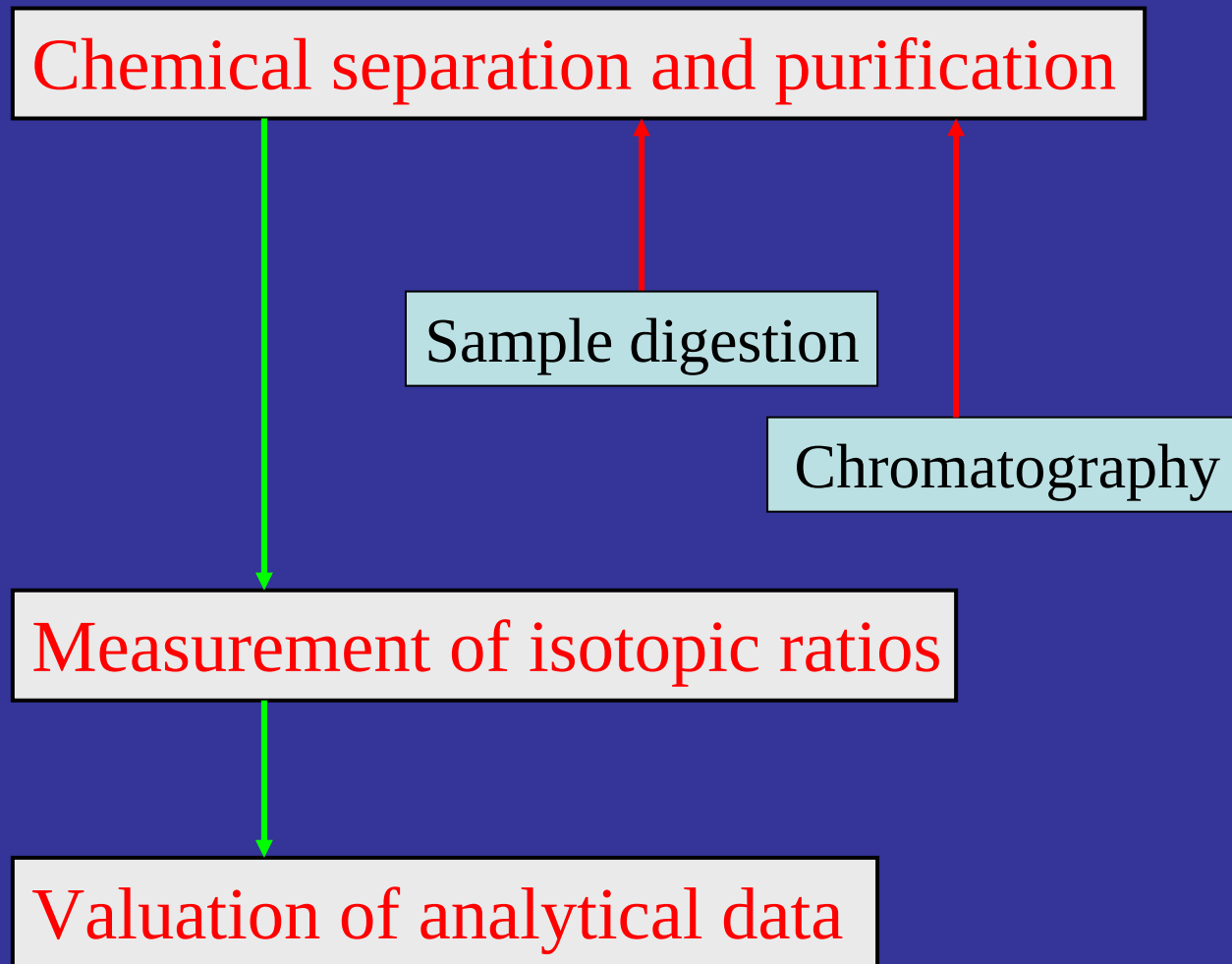
example: ^{87}Rb , $Z=37$, $N=50$

^{87}Sr , $Z=38$, $N=49$



放射成因同位素地球化学 实验方法与流程

Analytical procedure for isotopic geochemistry



超净化实验室环境下同位素分离纯化

为什么超净化环境？

- 样品中待分析组分含量低
- 降低环境和人为因素对样品的影响，
即降低实验室本底

如何尽可能降低本底？

- 净化实验室空气
- 净化化学试剂和器皿

质谱计基本原理与同位素比值测定

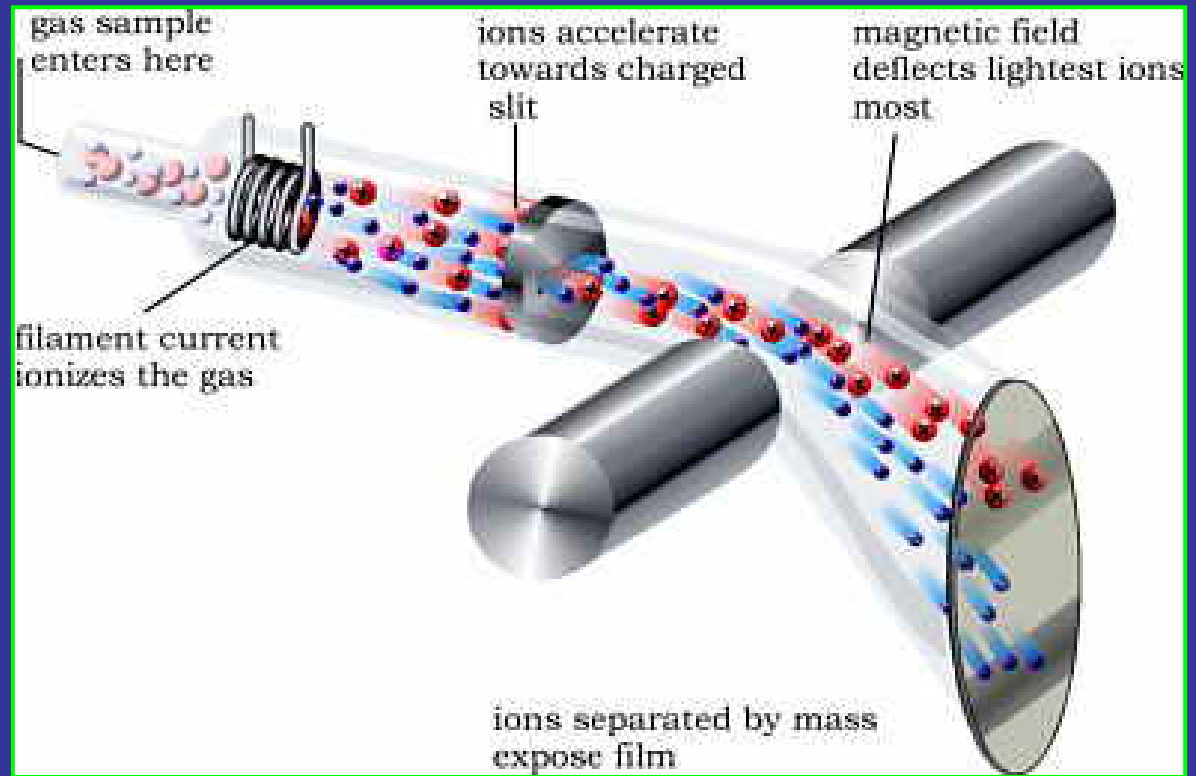
Mass spectrometer

- Device used to measure the mass of a given type of atom
- Mass spectrum:

Position of peaks give the atom mass

Relative heights of the peaks indicate relative number of atoms of different masses

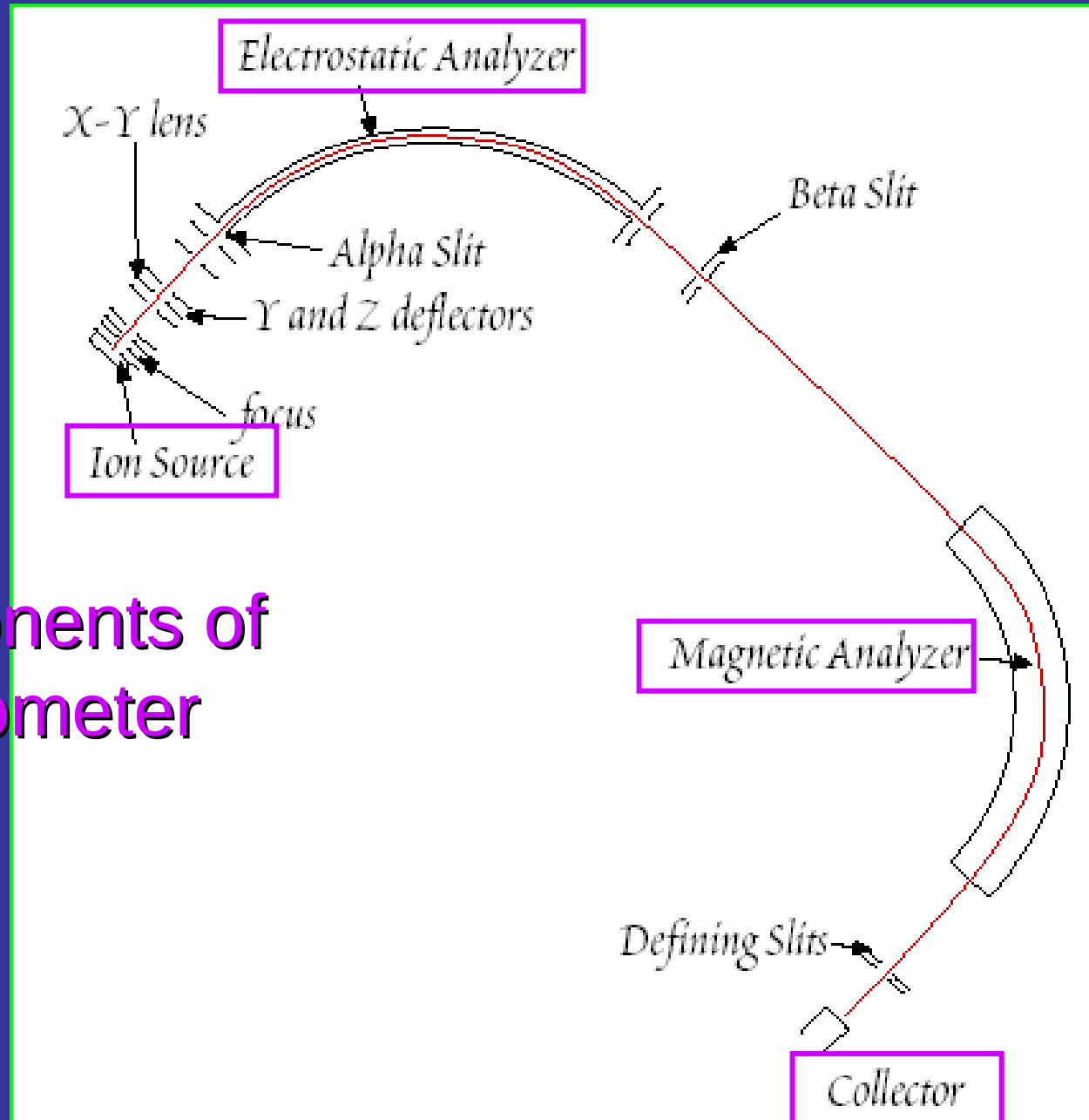
Charged Particle in Magnet Field

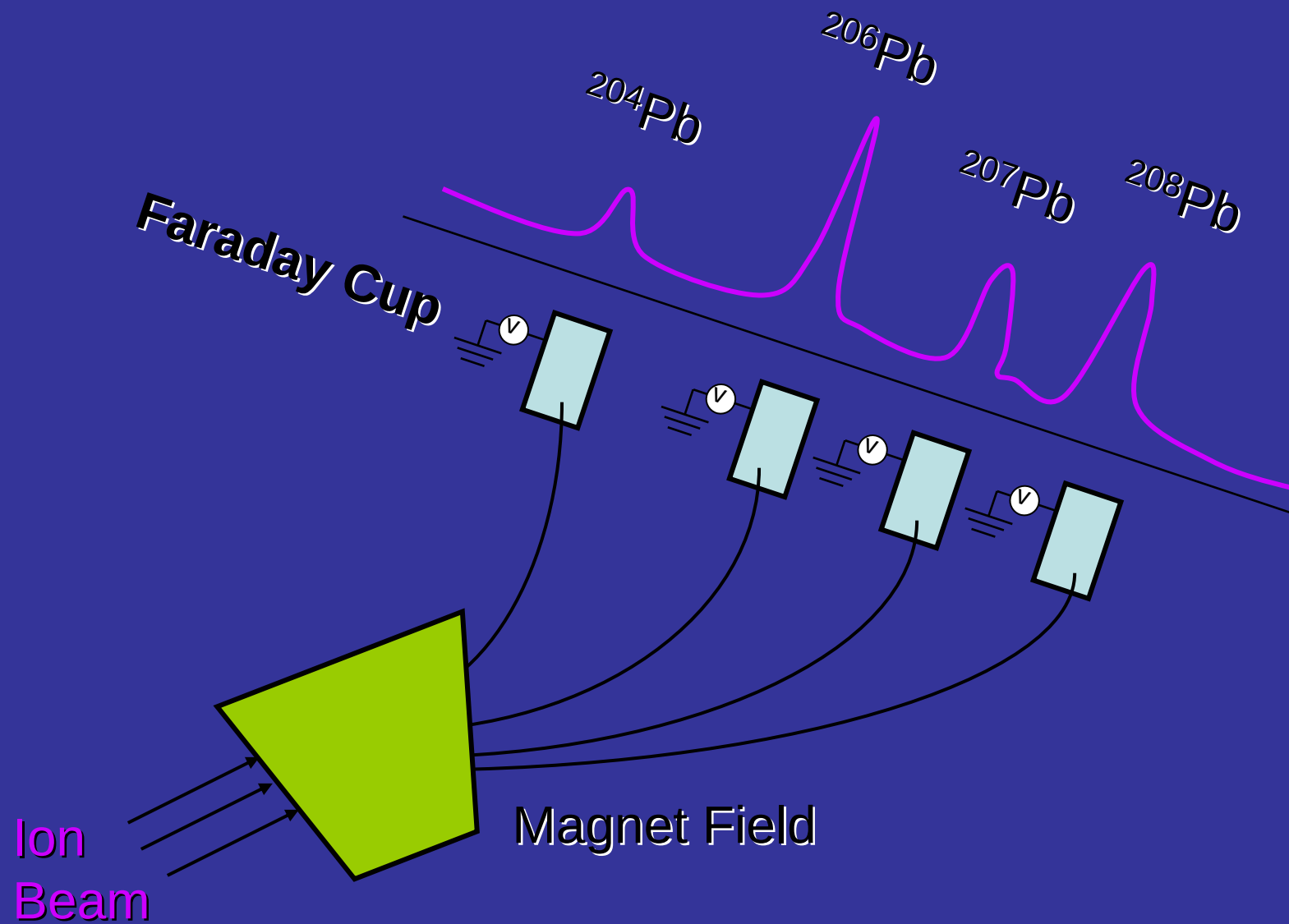


Mass/Charge ratio (m/q)

$$\frac{m}{q} = \frac{B^2 \cdot r^2}{2V}$$

Major Components of Mass Spectrometer





新型固体热电离质谱计

★ 德国Finnigan公司

TRITON

9个法拉第接收器，8个离子计数器

★ 英国 GV (Micromass)公司

IsoProbe-T

9个法拉第接收器，7个离子接收器

1个戴利接收器

英国GV公司IsoProbe-T

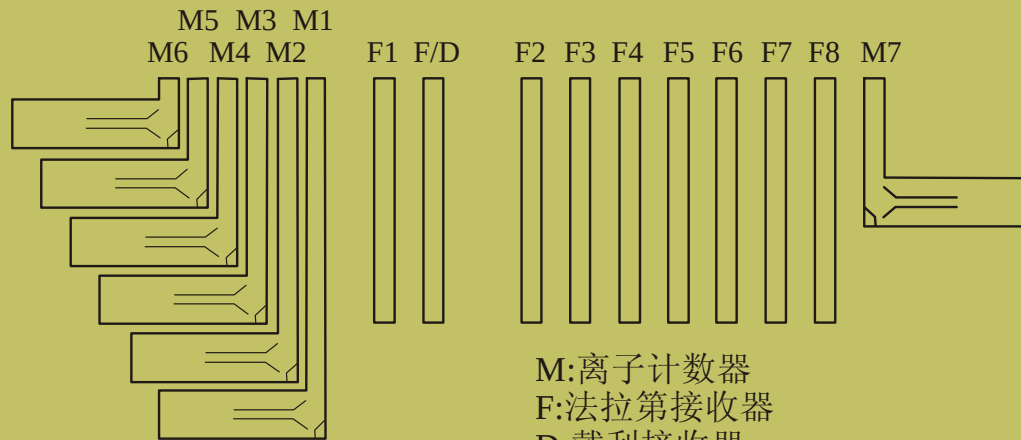


17 接收器:

9 个法拉第接收器

7 个离子计数器

1 个戴利接收器



M: 离子计数器
F: 法拉第接收器
D: 戴利接收器

Pb/U	206 208	204 207	208 210	238
Sr		84 85	86 87 88	
Nd		140 142	143 144 145 146 147 148 150	
U	234	235 236	238	
Th		230	232	



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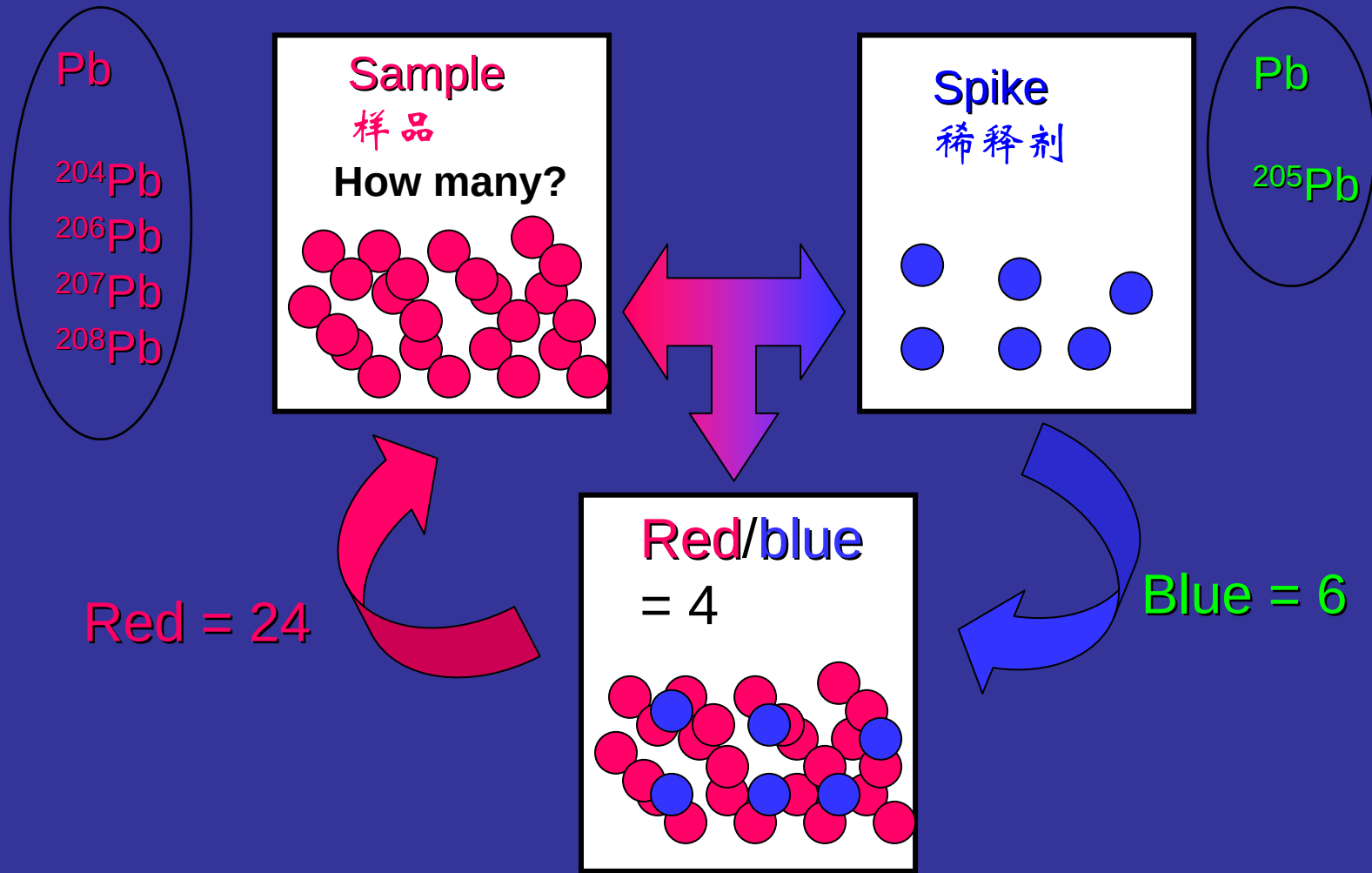
固体同位素地球化学实验室

同位素稀释法 (Isotope Dilution)

For dating or calculation of initial isotopic ratios, one has to know:

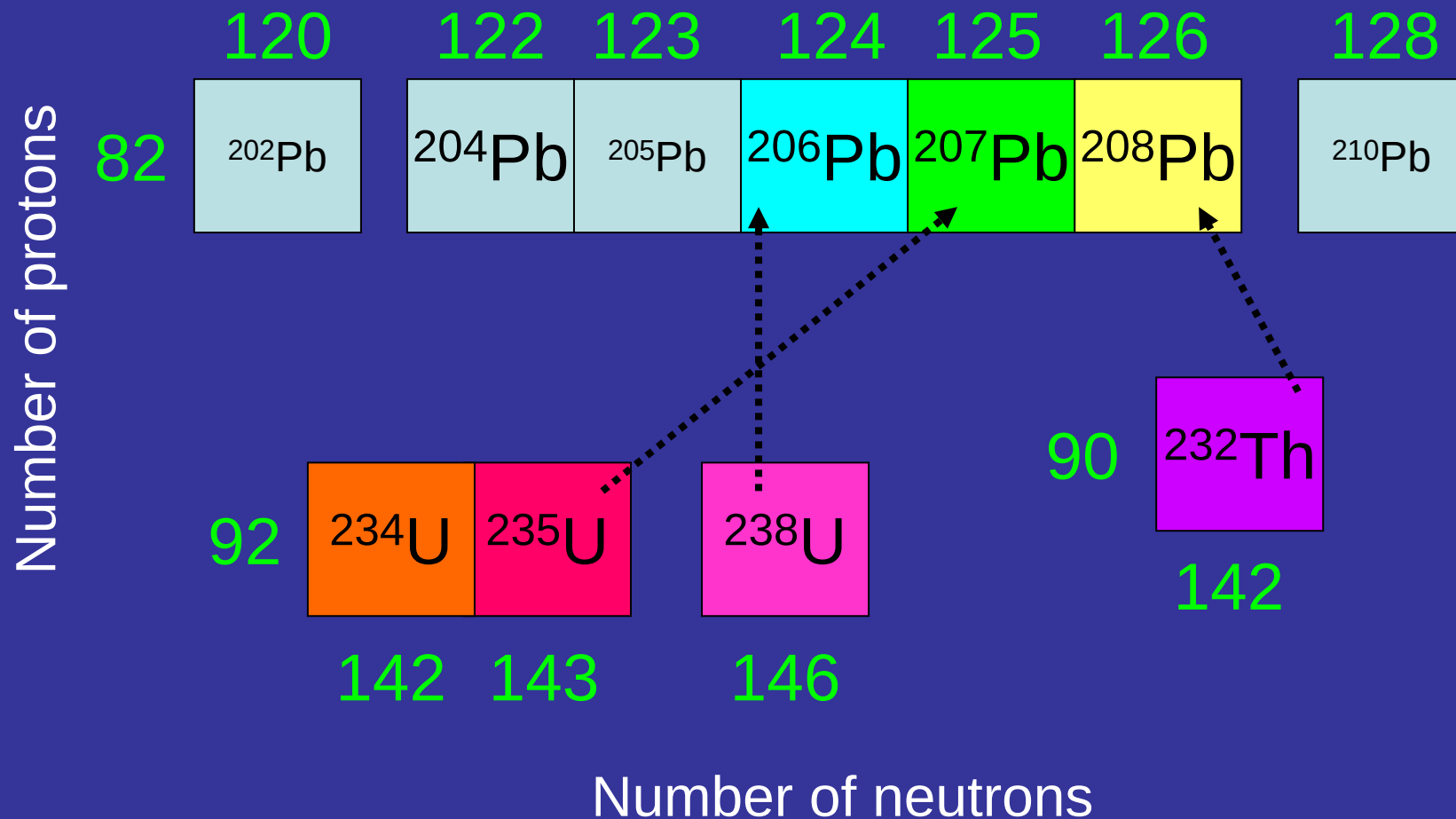
- Isotopic compositions of radioactive parent and its radiogenic product
- Their concentrations

How we can know the concentration?



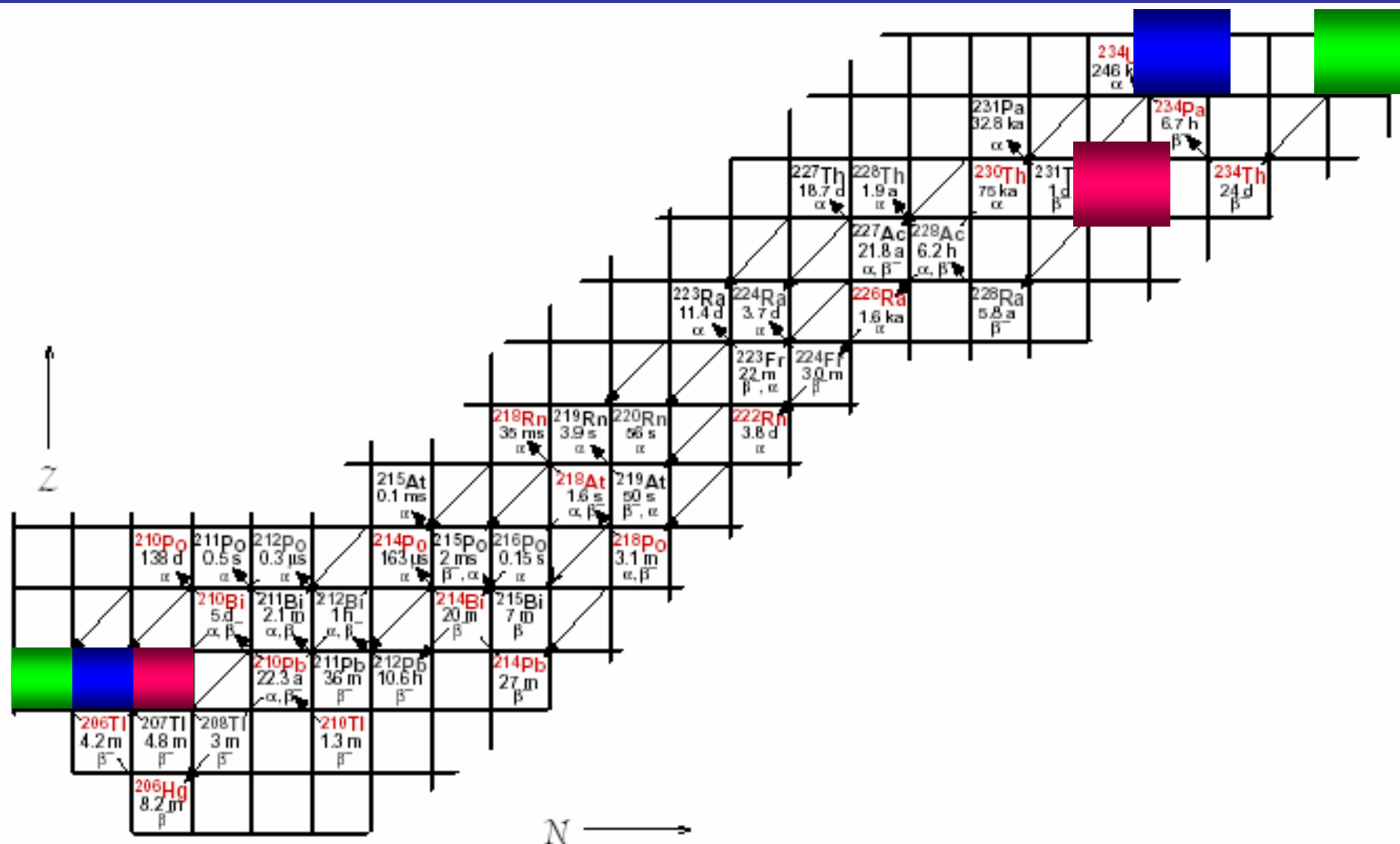
铀—铅定年方法

U – Th - Pb isotope system



U and Th Decay





Isotope abundance of U and Th

Group Ac (锕) metal, lithophile element and trace element in the Earth

Atomic abundance

^{234}U 0.0057%

^{235}U 0.720%

^{238}U 99.275%

^{232}Th 100%

Atomic abundance ratio:

$$^{238}\text{U}/^{235}\text{U} = 137.88$$

^{234}U is also radioactive,

$$T_{1/2} = 2.47 \times 10^5 \text{ (year)}$$

α -decay

Goldschmidt元素分类

Goldschmidt's Classification

GROUP

IA IIA IIIA IVA VA VIA VIIA VIIIA

1 H He

2 Li Be B C N O F Ne

3 Na Mg Al Si P S Cl Ar

4 K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr

5 Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe

6 Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn

7 Fr Ra Ac

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Ac Th Pa U Np Pu

Lithophile Siderophile Chalcophile Atmosphile

Pb Isotopes

Pb produced by radioactive decay of U and Th,



^{204}Pb is non-radiogenic

Increase of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ is due to U and Th decay.

Isotope abundance of Pb

Group IV metal, chalcophile element and trace element in the Earth

Atomic abundance

^{202}Pb		$T_{1/2} = \sim 3 \times 10^5 \text{ (year)}$
^{204}Pb	1.4%	$T_{1/2} = 1.4 \times 10^{17} \text{ (year)}$
^{205}Pb		$T_{1/2} = 3 \times 10^5 \text{ (year)}$
^{206}Pb	24.1%	
^{207}Pb	22.6%	
^{208}Pb	52.3%	
^{210}Pb		$T_{1/2} = 22 \text{ (year)}$

Both U and Th generally have a valence of +4, but under oxidizing conditions, U may have a valence of +6.

U^{4+} has an ionic radius of 0.89Å and U^{6+} has an ionic radius of 0.73Å in 6-fold and 0.86Å in 8-fold coordination. Th has an ionic radius of 0.94Å.

Combination of relatively large radius and high-charge is not readily accommodated in crystal lattices of most common rock-forming minerals, so both U and Th are highly incompatible elements.

Th is relatively immobile under most circumstances.

In its reduced form, U^{4+} is insoluble, but in the U^{6+} form, U forms the soluble oxyanion complex, UO_2^{2-} , and then U can be quite mobile.

U and Th can form their own phases in sedimentary rocks, uranite and thorite

In igneous and metamorphic rocks, U and Th are either dispersed as trace elements in major phases or concentrated in accessory minerals:

Zircon (ZrSiO_4), U > Th

Monazite ($[\text{La,Ce,Th}]\text{PO}_4$), Th > U

Apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$)

Sphene or titanite ($\text{CaTi}(\text{SiO}_4)\text{OH}$)

Pb can exist in two valence states, Pb^{2+} and Pb^{4+} . Pb^{2+} is the most common state and Pb^{4+} state is rare and restricted to highly alkaline or oxidizing solutions.

The ionic radius of Pb^{2+} is $1.19\text{\AA}$ in 6-fold coordination and $1.29\text{\AA}$ in 8-fold coordination.

As a result of its large ionic size, Pb is an incompatible element, though not as incompatible as U and Th.

The most common Pb mineral is galena (PbS). In silicates, Pb substitutes reasonably readily for K (ionic radius 1.33), particularly in potassium feldspar.

$$^{207}\text{Pb}^* = ^{235}\text{U}(e^{\lambda 5t} - 1)$$

$$^{206}\text{Pb}^* = ^{238}\text{U}(e^{\lambda 8t} - 1)$$

$$\begin{aligned} \frac{^{207}\text{Pb}^*}{^{206}\text{Pb}^*} &= \frac{^{235}\text{U}(e^{\lambda 5t} - 1)}{^{238}\text{U}(e^{\lambda 8t} - 1)} \\ &= \frac{1}{137.88} \frac{(e^{\lambda 5t} - 1)}{(e^{\lambda 8t} - 1)} \end{aligned}$$

U-Pb表面年龄

$$t_{206\text{Pb}/238\text{U}} \quad t_{207\text{Pb}/235\text{U}} \quad t_{207\text{Pb}/206\text{Pb}}$$

谐和年龄（一致年龄）

$$t_{206\text{Pb}/238\text{U}} = t_{207\text{Pb}/235\text{U}} = t_{207\text{Pb}/206\text{Pb}}$$

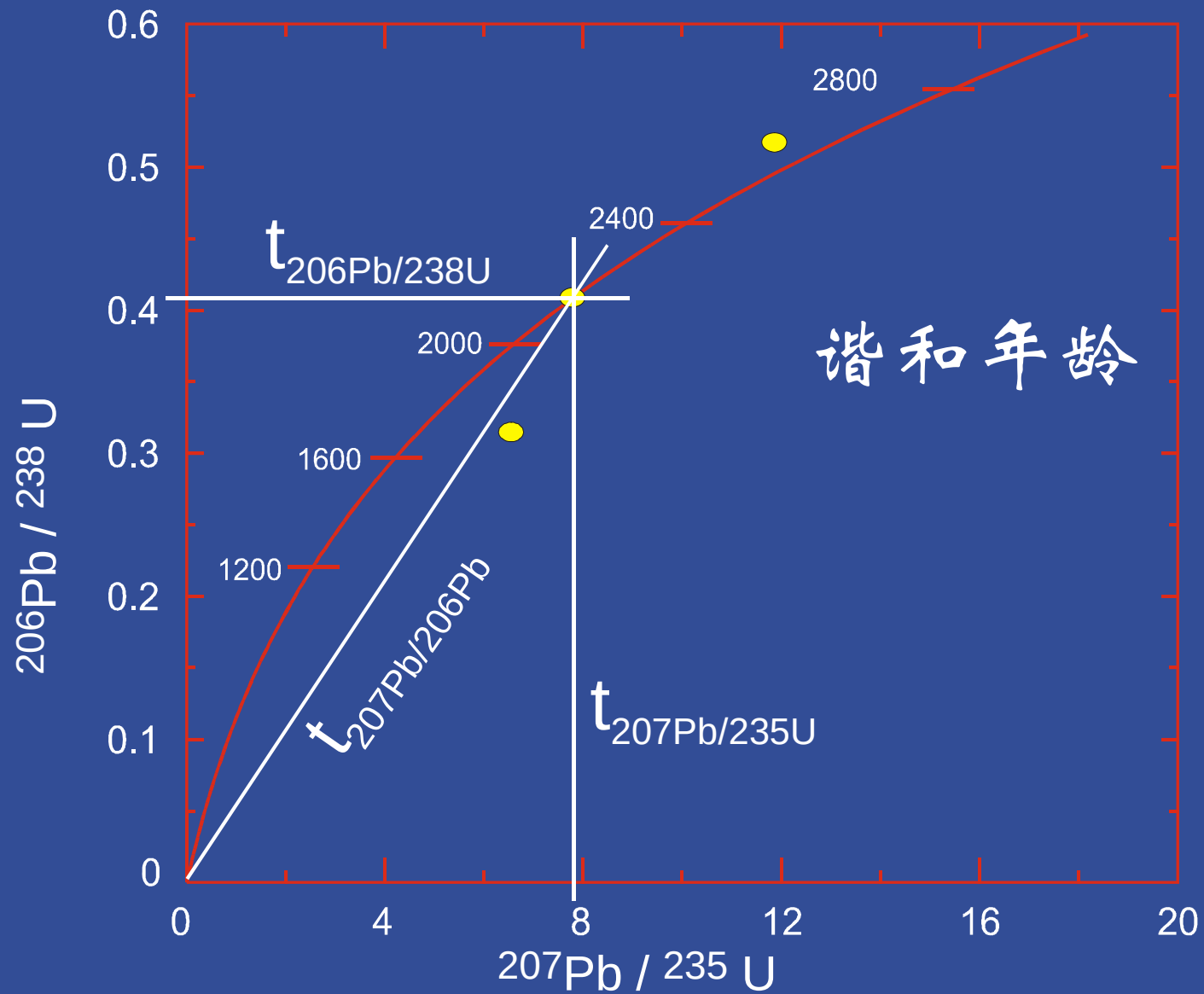
不谐和年龄

$$t_{206\text{Pb}/238\text{U}} < t_{207\text{Pb}/235\text{U}} < t_{207\text{Pb}/206\text{Pb}}$$

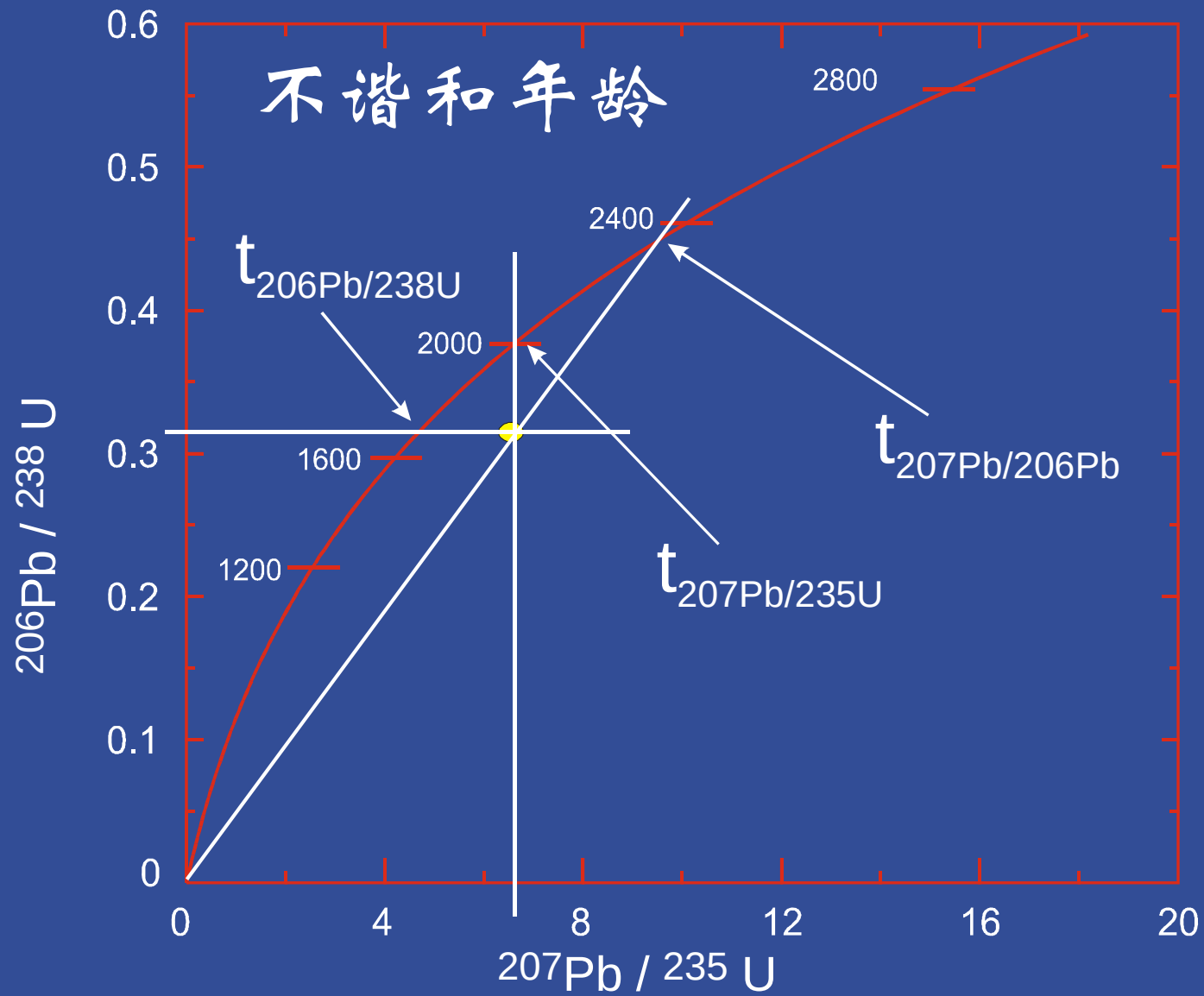
反相不谐和年龄

$$t_{206\text{Pb}/238\text{U}} > t_{207\text{Pb}/235\text{U}} > t_{207\text{Pb}/206\text{Pb}}$$

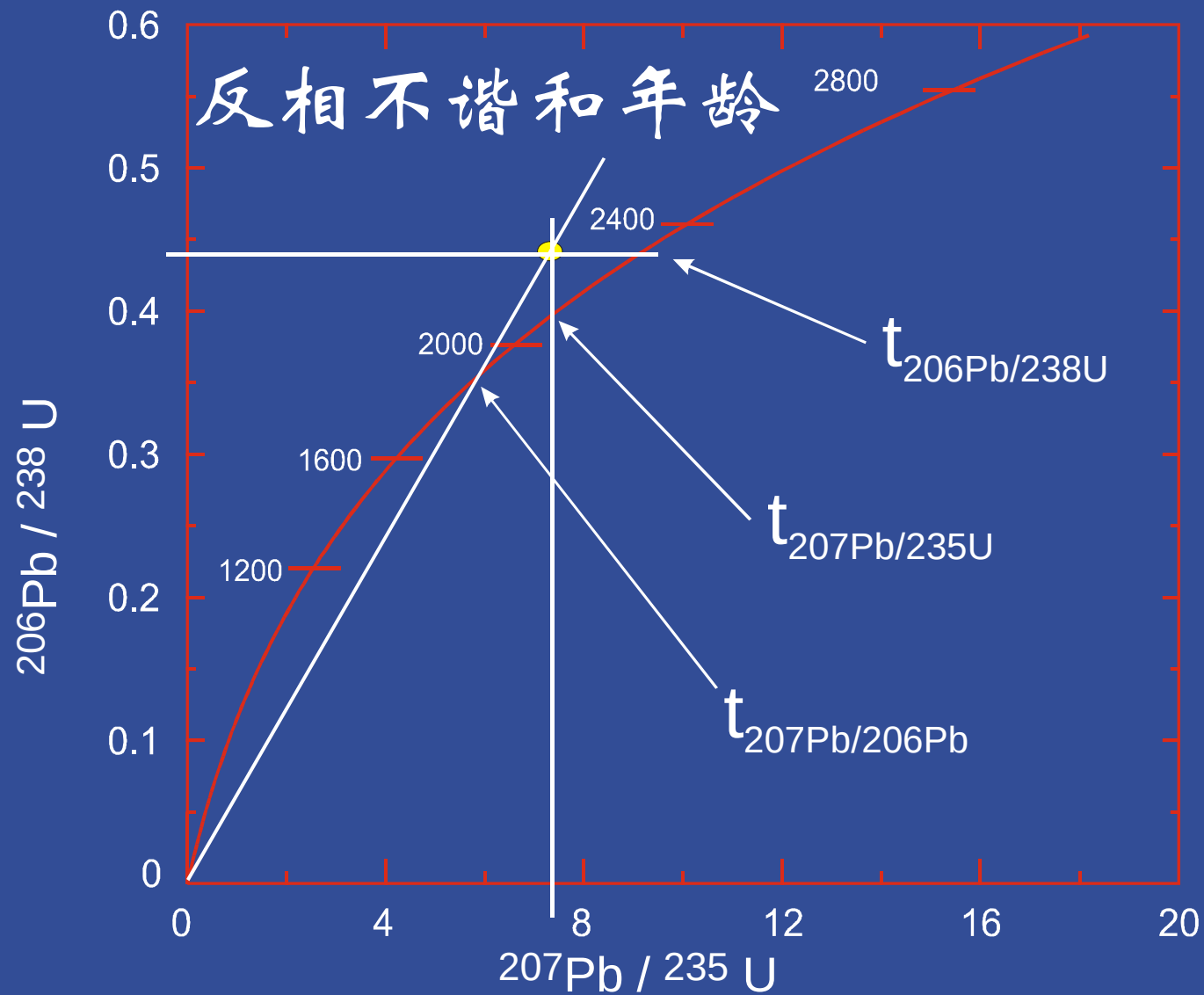
U – Pb concordia diagram



U – Pb concordia diagram



U – Pb concordia diagram

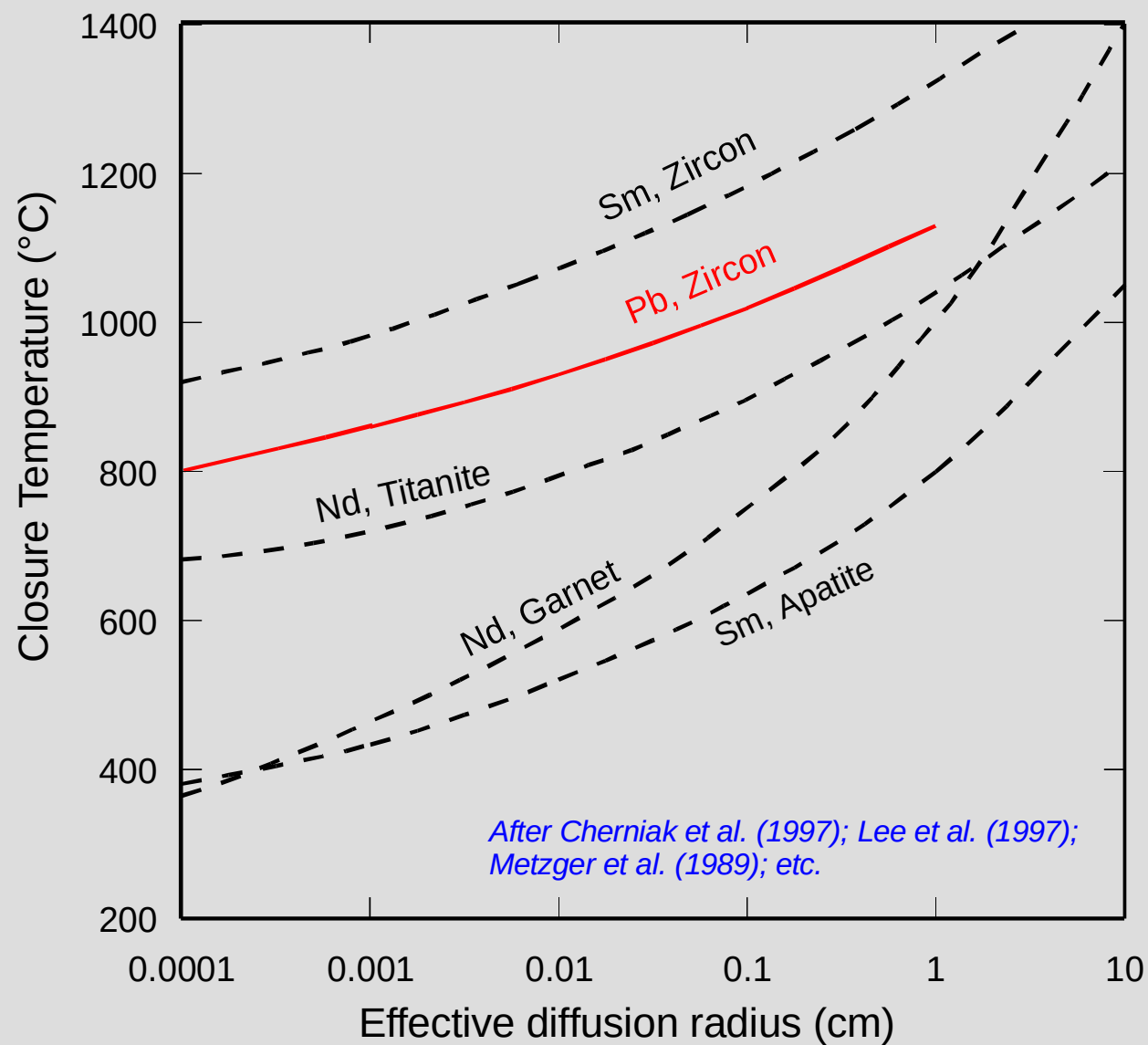


锆石 Zircon $Zr[SiO_4]$

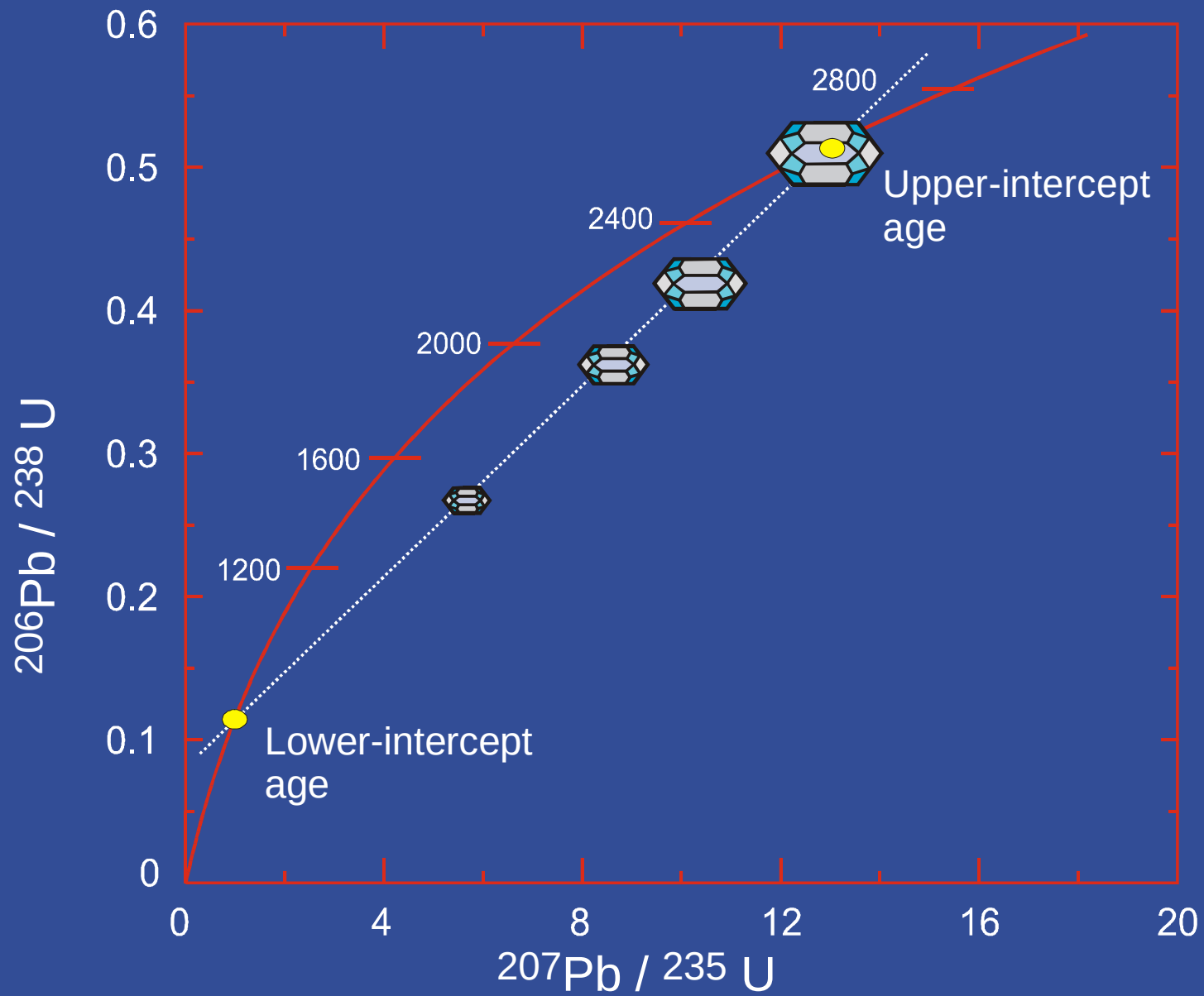
- Hf (ca. 1%)
- REE
- appreciable U and Th



U – Pb同位素体系封闭温度



U-Pb concordia diagram

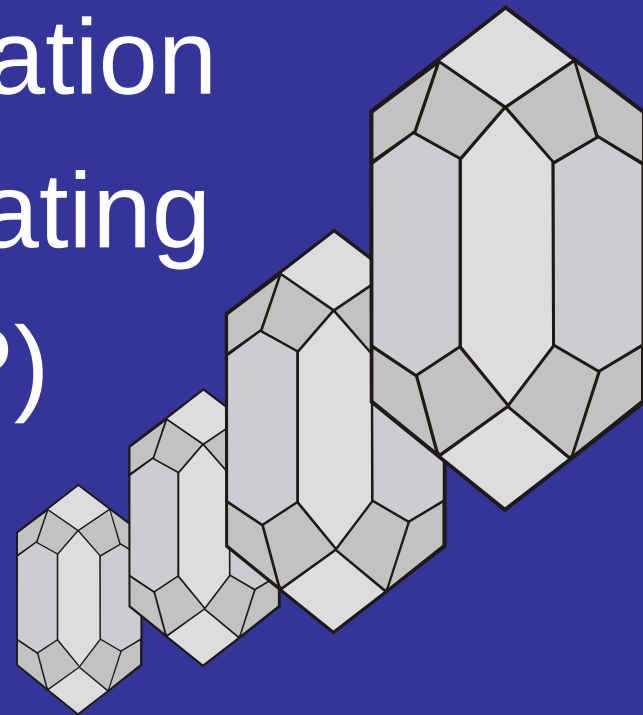


有效地获得谐和的U-Pb表面年龄的方法

1. 机械磨损法 (Krogh, 1982)
2. 逐步酸淋滤法或称局部溶解法 (Mattinson, 1994)
3. 单颗粒蒸发法 (Kober, 1986, 1987)
4. 阴极发光指导选样法 (Poller et al., 1997)
5. 机械晶区分离法 (Sergeev et al., 1997)
6. 离子探针微区分析 (Compston et al., 1984)

Zircon dating

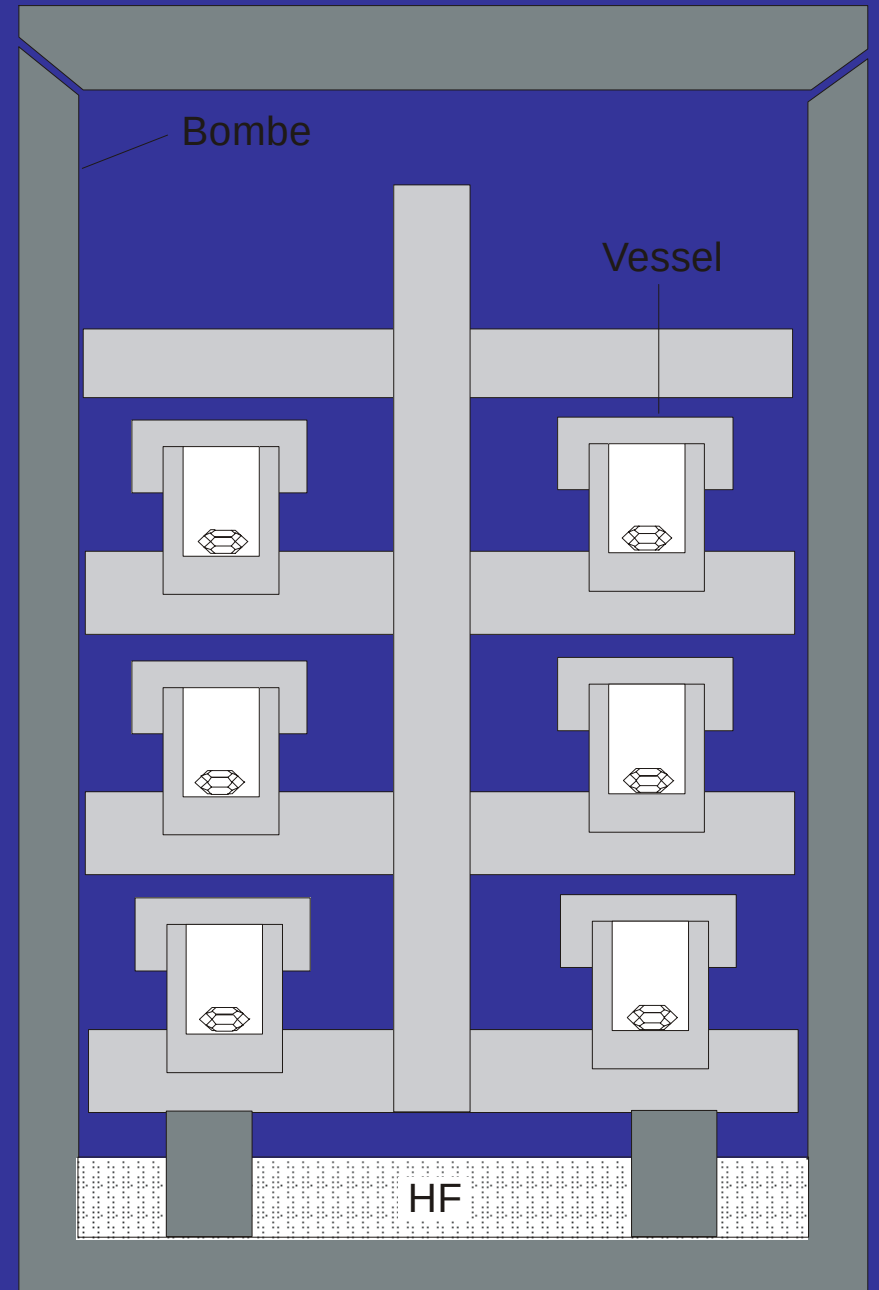
- U-Pb isotope dilution
- Pb-Pb evaporation
- *in-situ* U-Pb dating
(e.g., SHRIMP)



Chemical Procedure

Zircon U-Pb isotope dilution

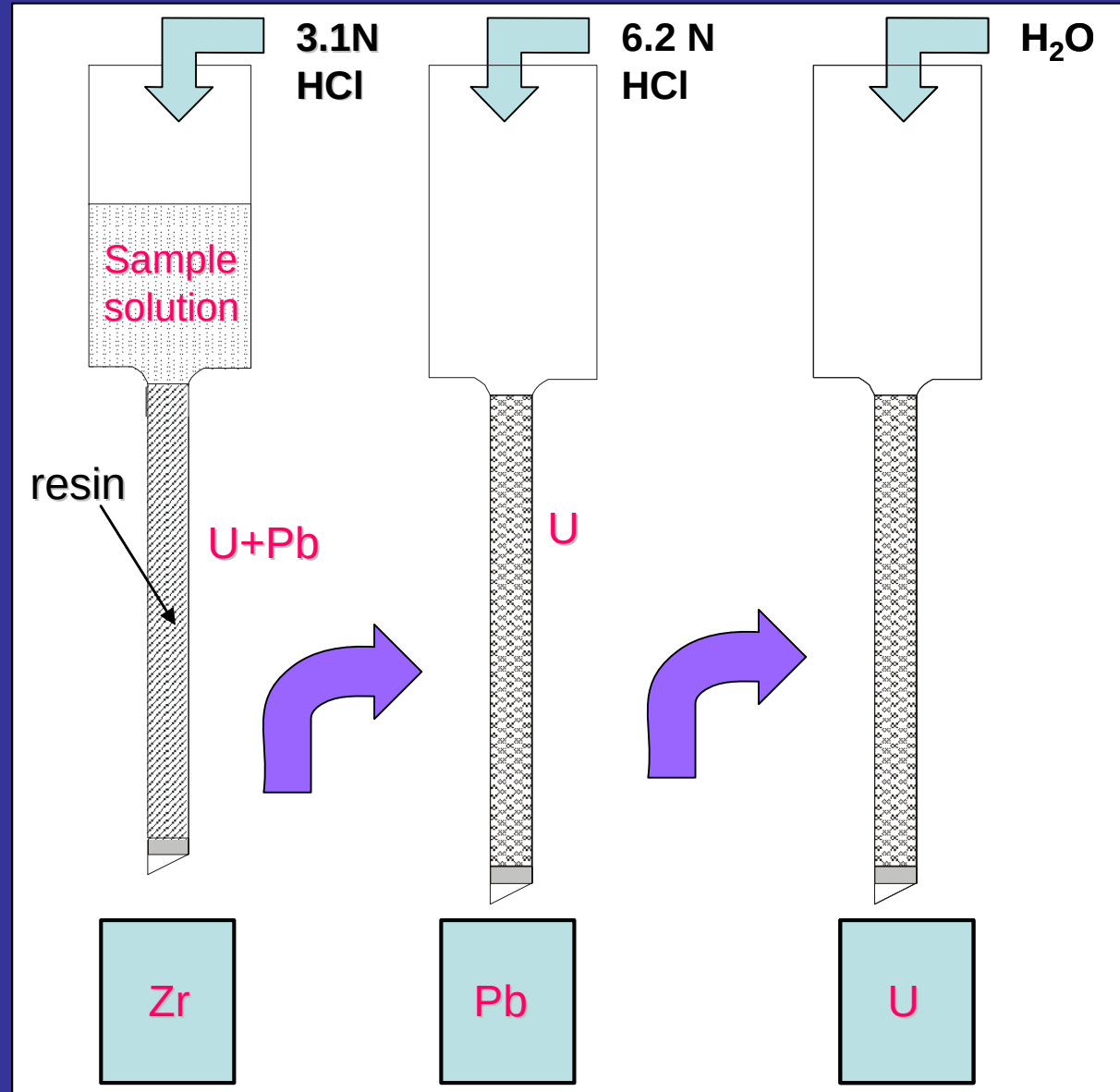
1. Decomposition of zircon grains



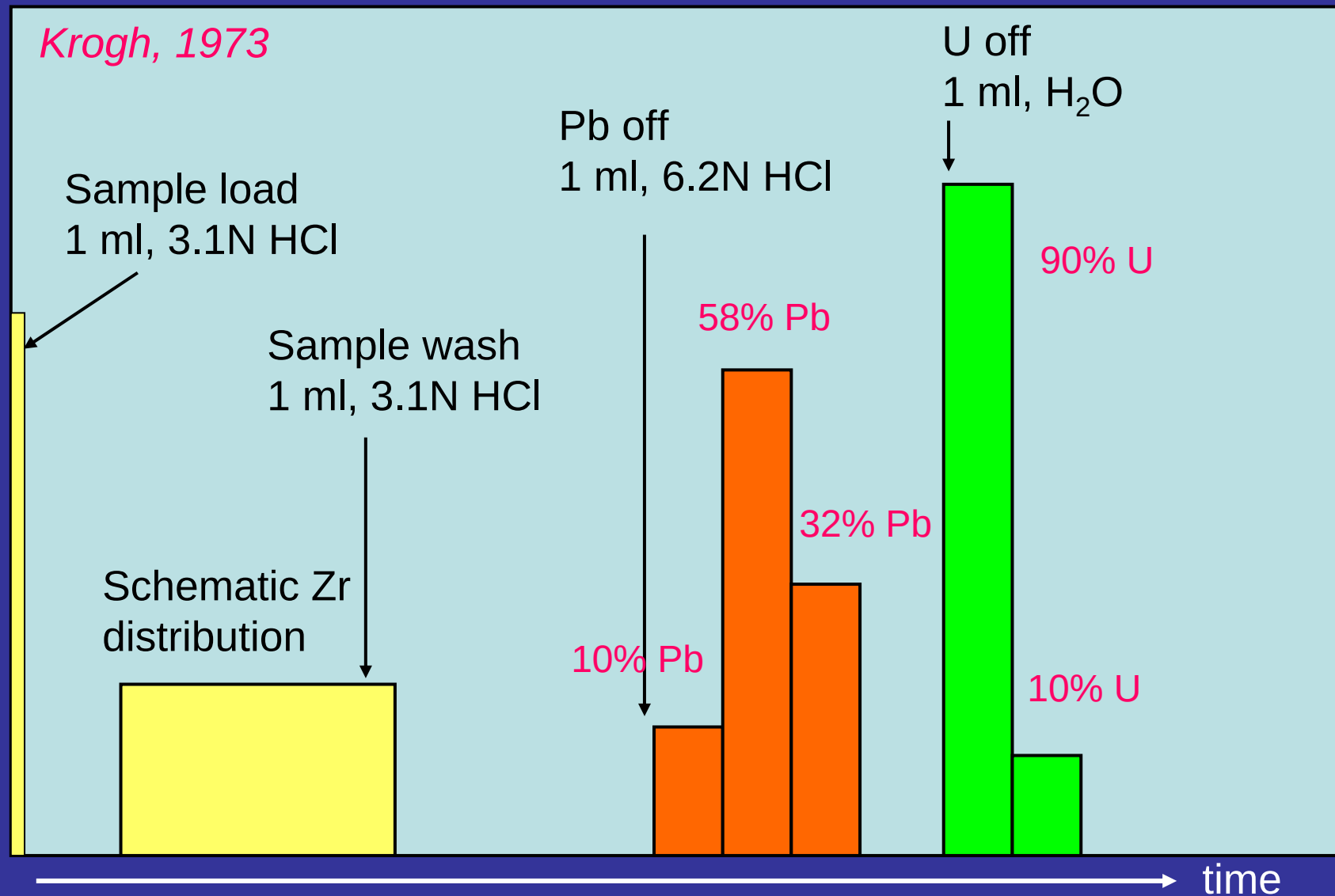
Chemical Procedure

Zircon U-Pb isotope dilution

2. Separation of U and Pb (HCl)

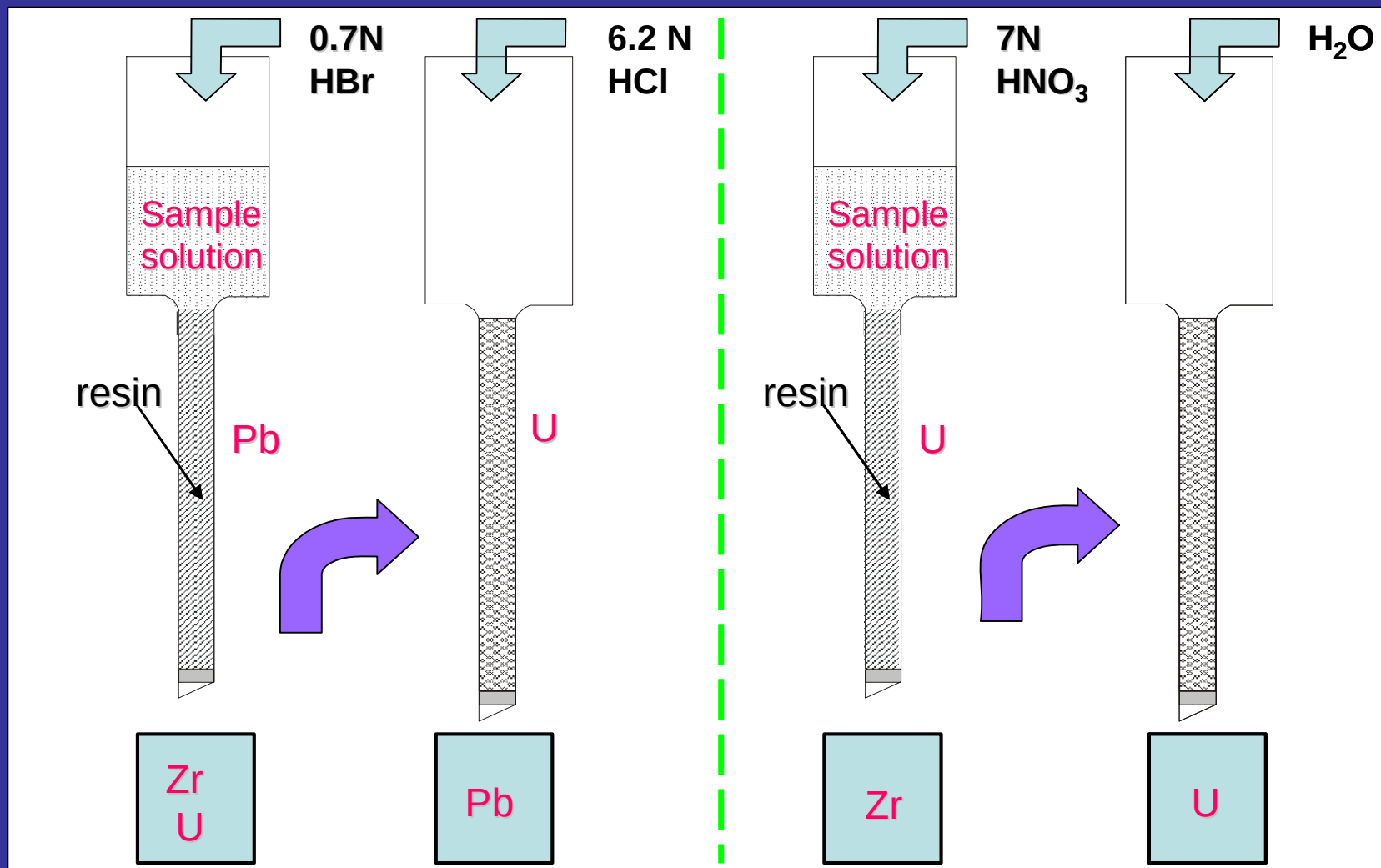


Ion exchange elution curves of Zr, Pb and U



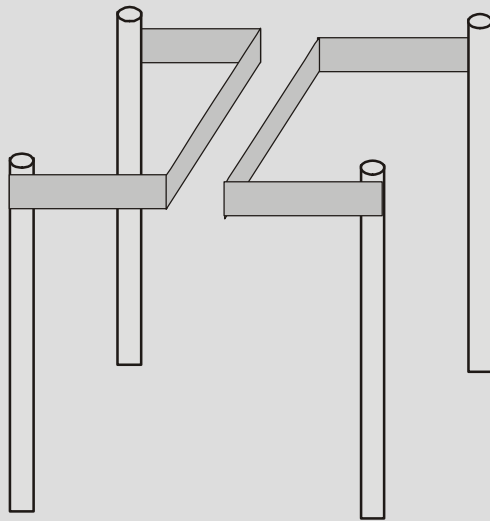
Chemical Procedure

Separation of U and Pb (HBr & HNO₃)

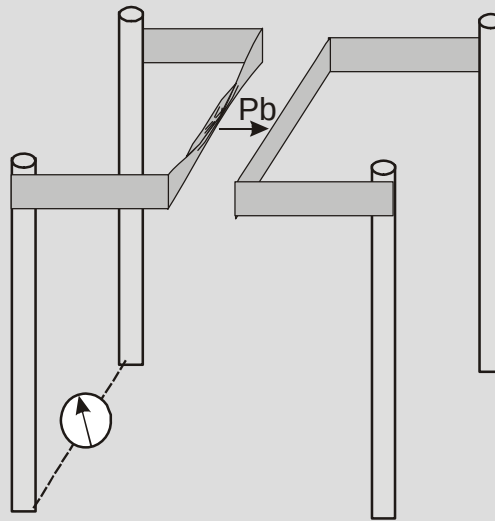


Dating Zircon by Evaporation Method

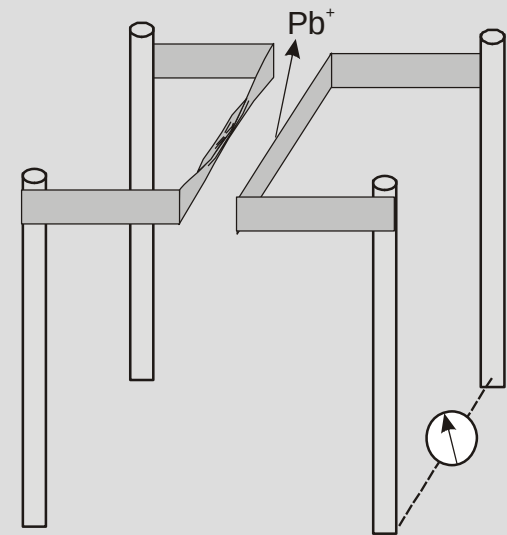
1. Pack zircon
in filament



2. Evaporate
zircon

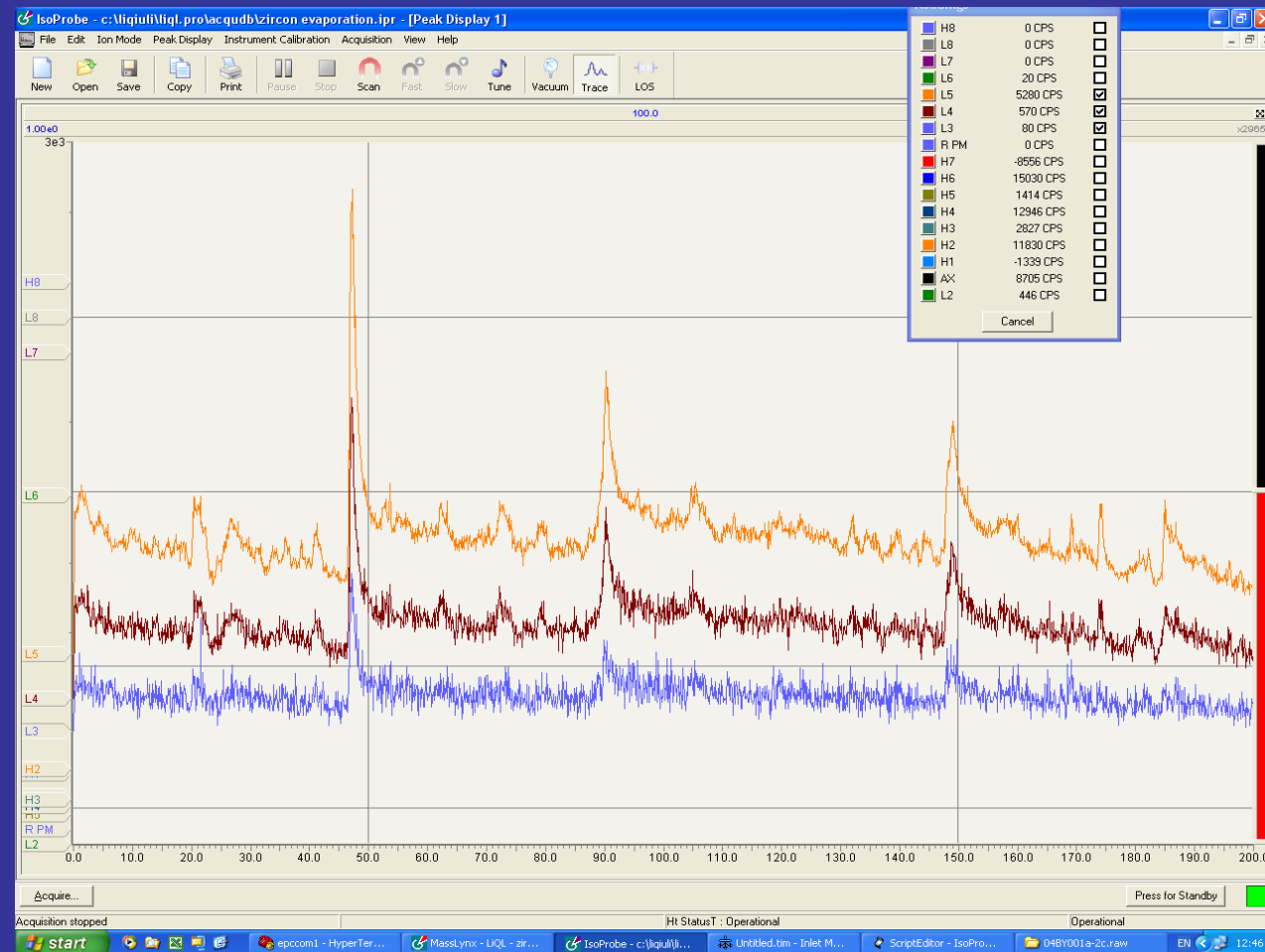


3. Measure Pb
isotopes



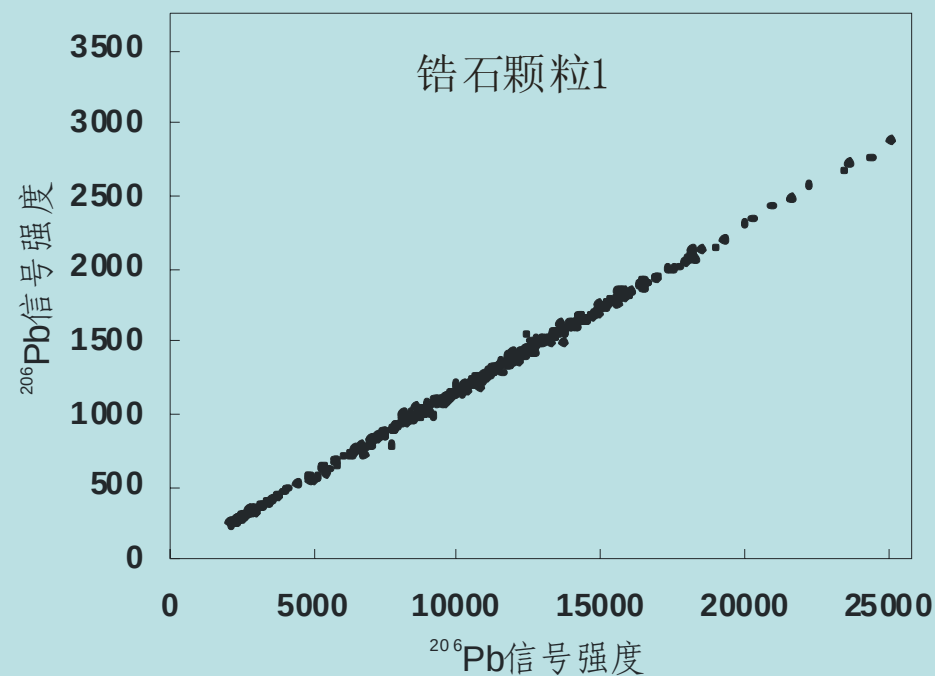
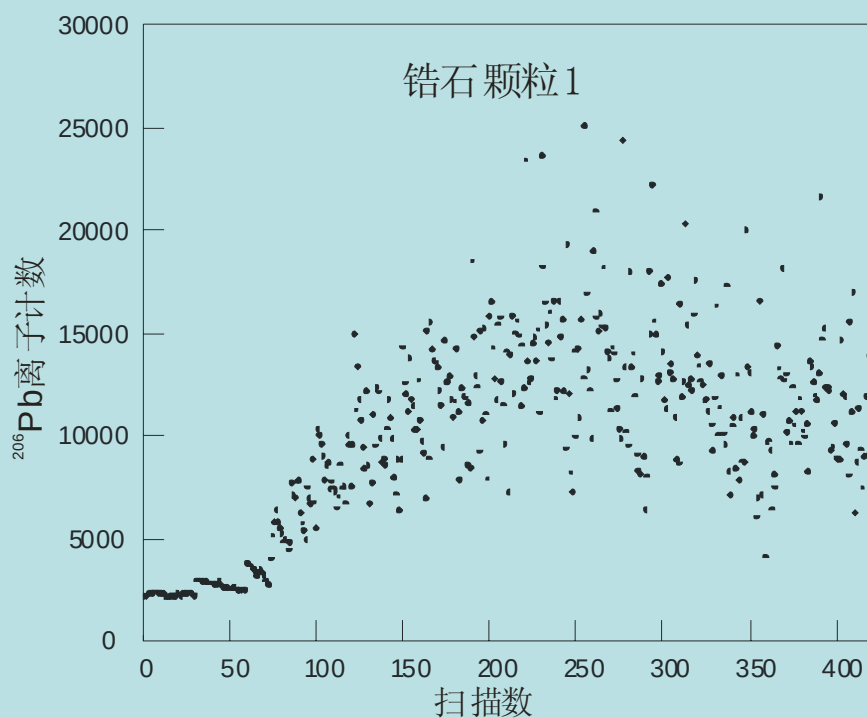
4. Repeat steps 2 & 3

锆石蒸发法：即时信号随时间变化较强
单接收器难以实现即时测量Pb同位素比值
多个离子计数器可以实现静态测量

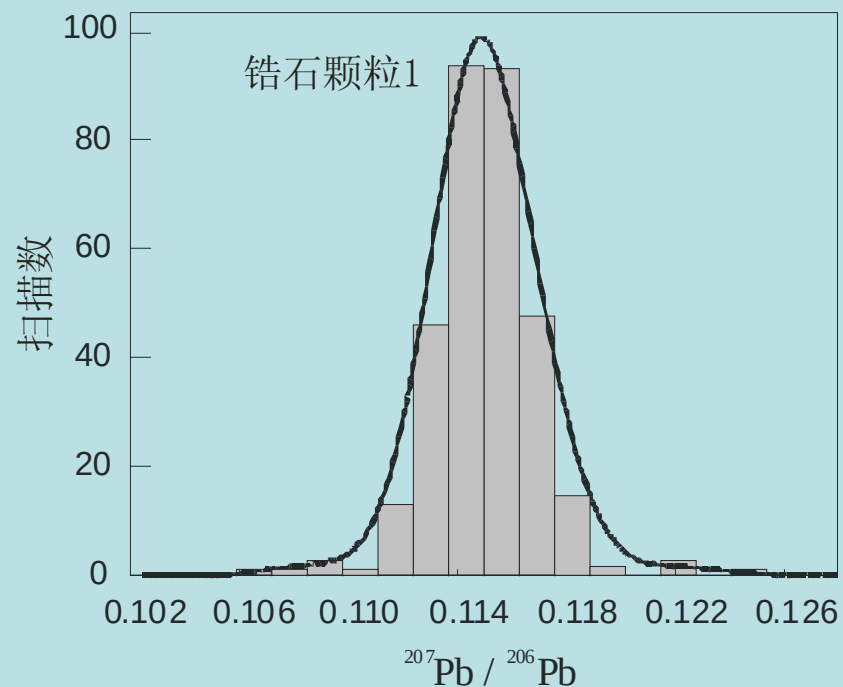


锆石加热蒸发时， ^{206}Pb
信号强度变化幅度大

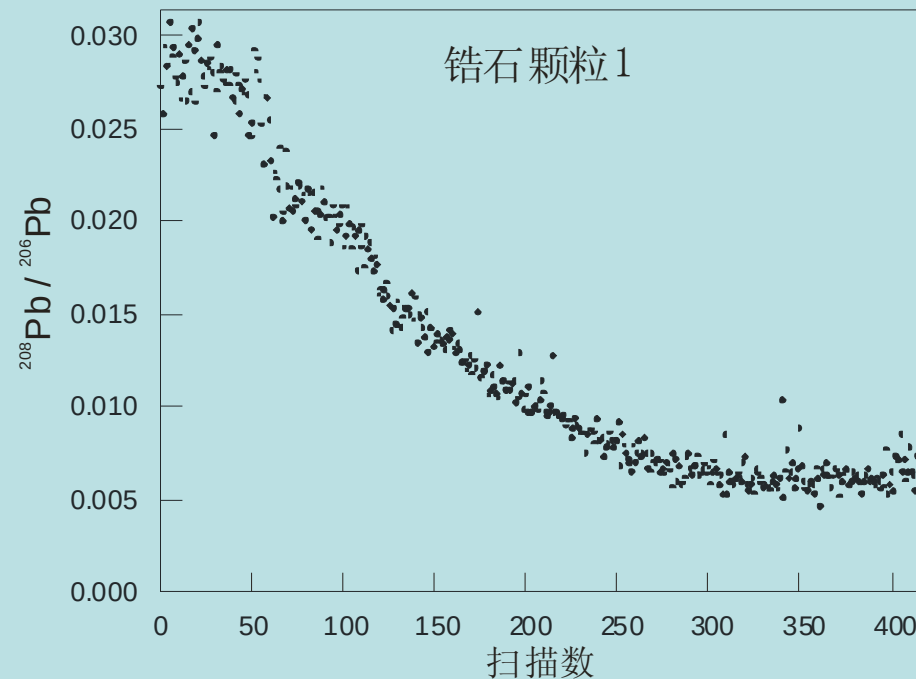
^{206}Pb 和 ^{207}Pb 信号强度变
化具有线性关系，暗示
没有铅丢失



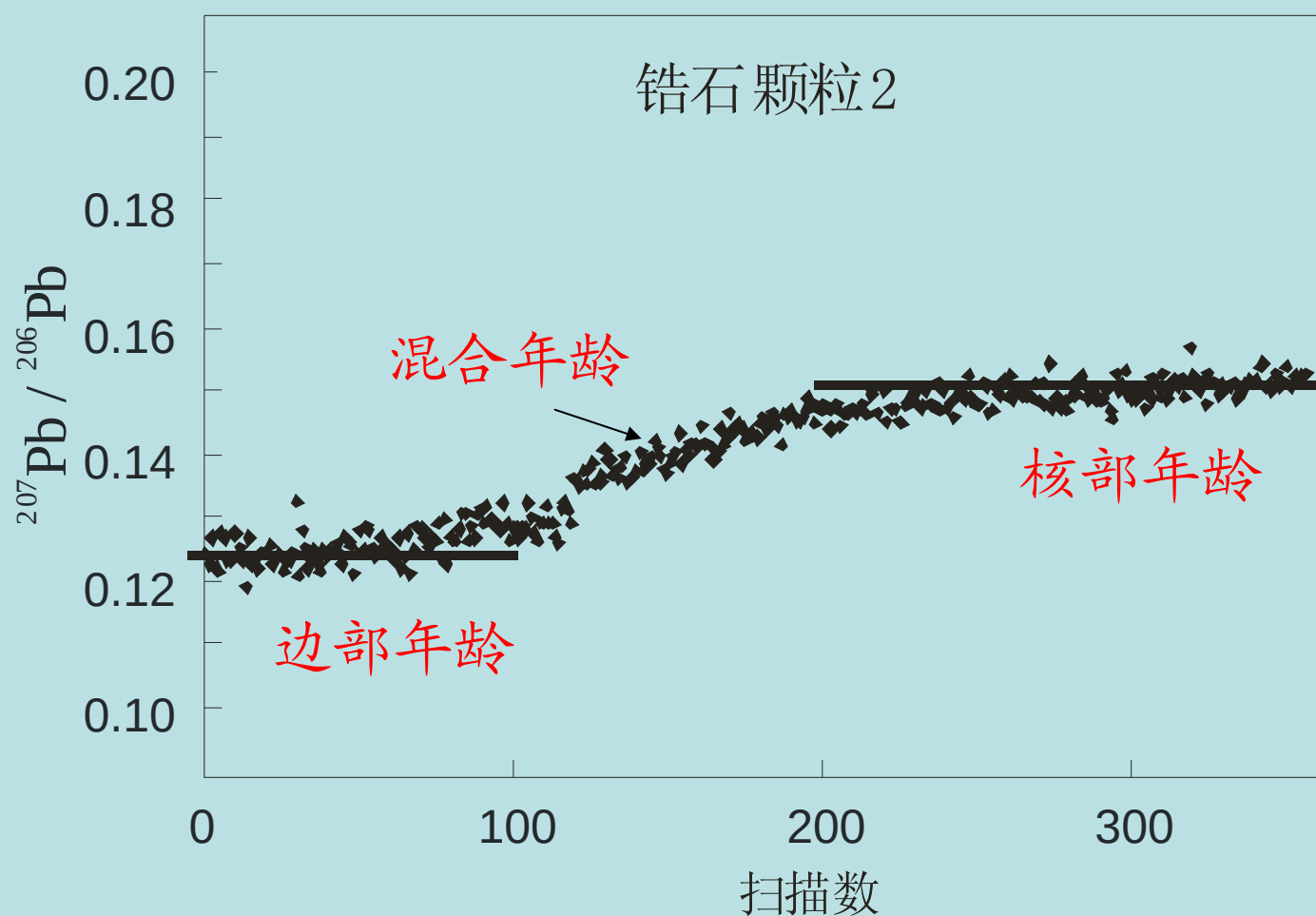
锆石蒸发法 $^{207}\text{Pb}/^{206}\text{Pb}$
比值正态分布，暗示
具有谐和U-Pb年龄



锆石蒸发法 $^{208}\text{Pb}/^{206}\text{Pb}$
比值变化，反映锆石
内部Th/U环带



锆石蒸发法 $^{207}\text{Pb}/^{206}\text{Pb}$ 比值变化，反映锆石具有复杂演化历史，如核边内部结构、铅部分丢失、或继承锆石等



Zircon dating methods

- U-Pb method

(traditional and single-grain)

Total Pb- and U-blank:

~ 1-20 pg

suitable minerals:

zircon, sphene, monazite, ...

age range:

from Cenozoic to Archean

- Evaporation method

Total Pb- and U-blank:

0 pg

suitable minerals:

zircon

age range:

from Mesozoic to Archean

In-situ zircon dating

- SHRIMP
- SIMS
- MC-ICP-MS
- LA-ICP-MS

离子探针方法

直观地获得分析锆石微区（in-situ）的Pb同位素组成和U/Pb比值和U-Pb年龄

基本原理：采用轻离子束，如 O^+ 离子，轰击抛光的锆石晶区，产生Pb的二次离子束，然后通过一个电场和磁场双重聚焦的质谱计分析而获得Pb同位素组成

这一分析方法简称为SIMS方法，Secondary Ion Mass Spectrometer

SIMS主要问题是，轰击溅出的其它带电分子干扰待分析同位素的测量，即同质异素干扰

克服这一干扰问题，需要提高质谱计的质量分辨率

核素间的结合能不同导致不同原子结合而成的分子之间存在微细小质量差异。通过增大质谱计的体积，主要加大磁场，将质量分辨率提高到可以区分这样微细质量差异的不同分子

上世纪80年代，澳大利亚研制成SHRIMP离子探针
(Sensitive High-Resolution Ion Micro-Probe)

Sensitive High Resolution Ion Micro-Probe (SHRIMP)



Applications

- **Geochronology**

igneous rock, metamorphism overgrowth,
provenance of magma or sediments

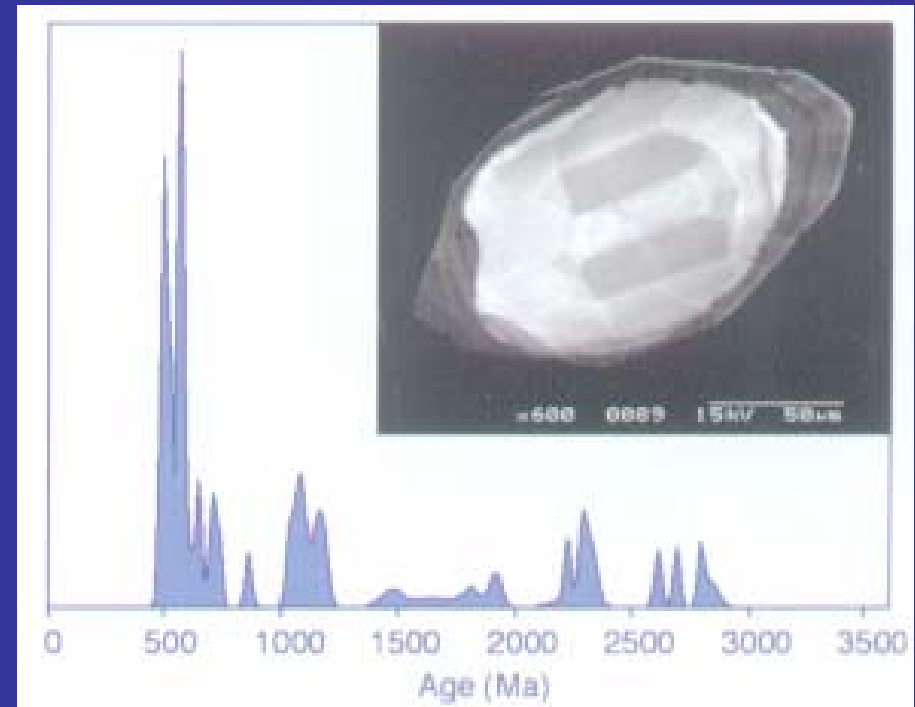
- **Stable Isotope Geochemistry**

- **Isotope Anomalies**

anomalies in refractory meteoritic minerals

- **Trace element geochemistry**

profiling rare earth elements,
isotope imaging

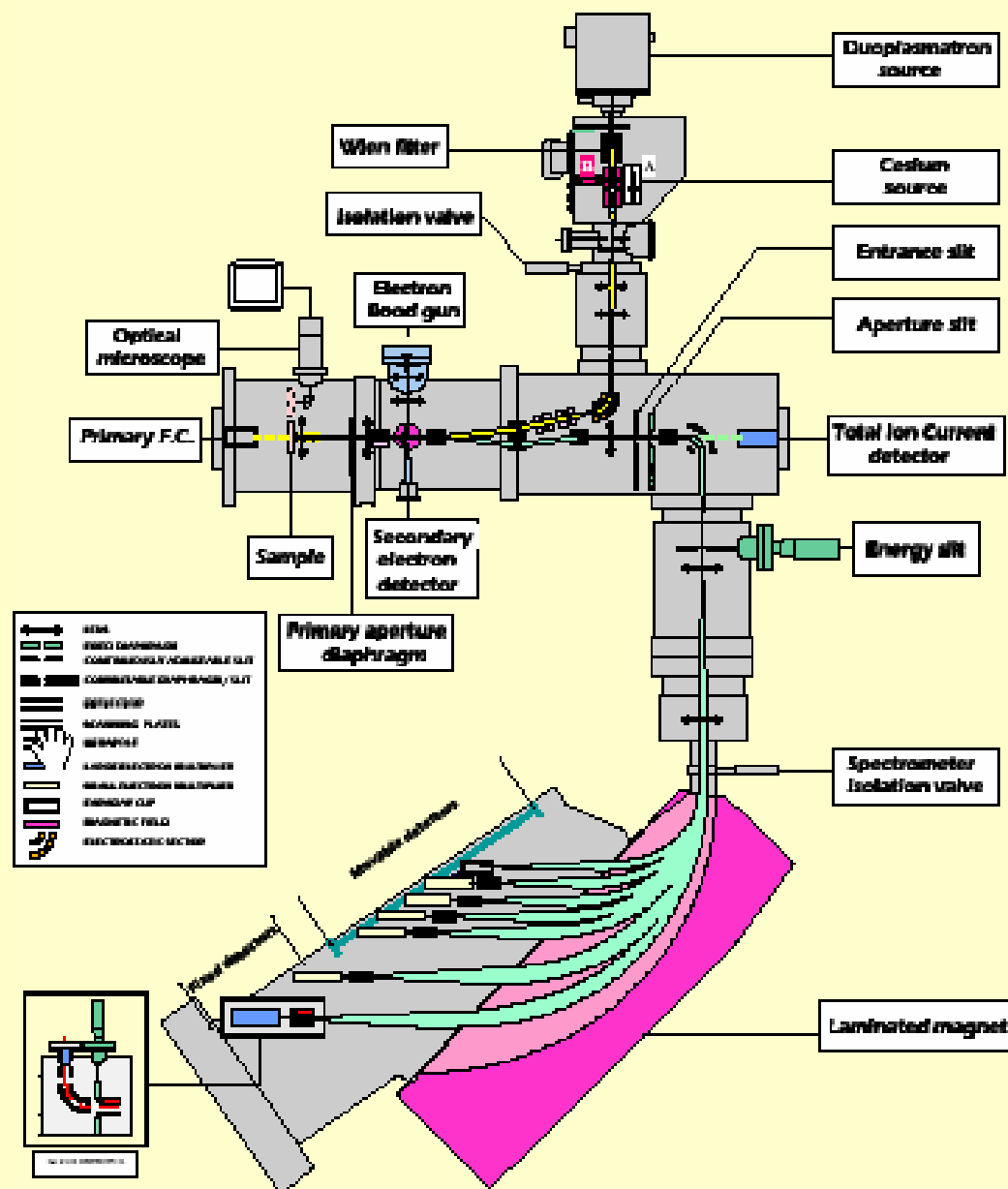


Secondary Ion Mass Spectrometry (SIMS)



CAMECA

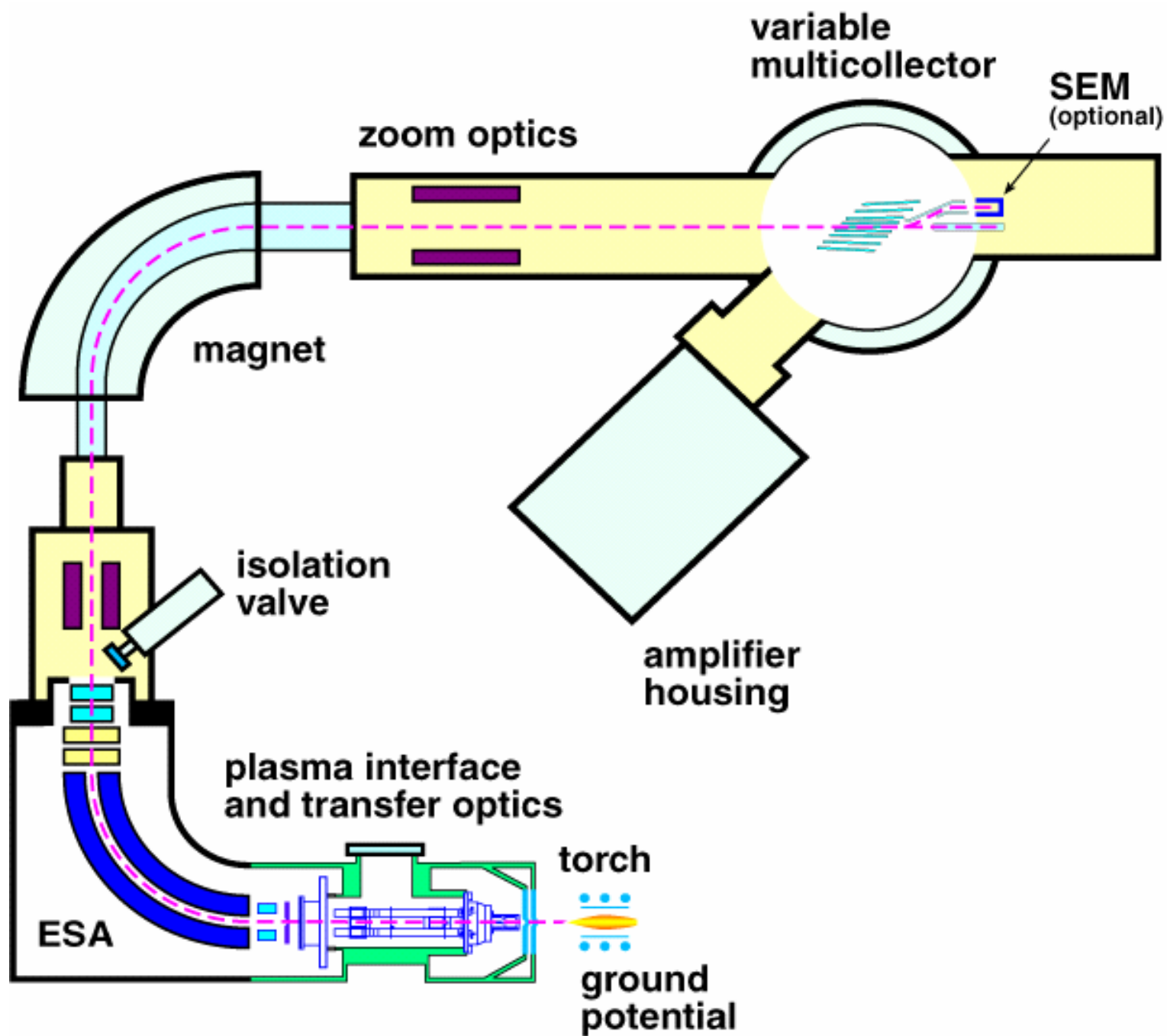
NANOSIMS 50



Multi-collector ICP- MS

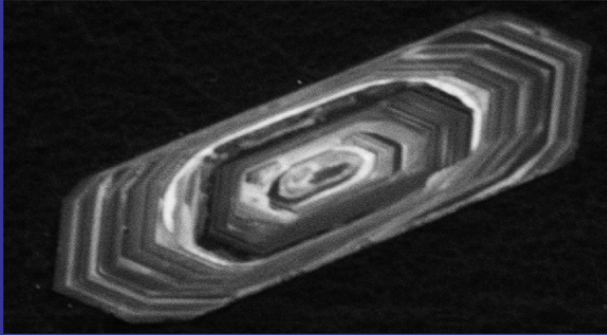


Finnigan MAT NEPTUNE

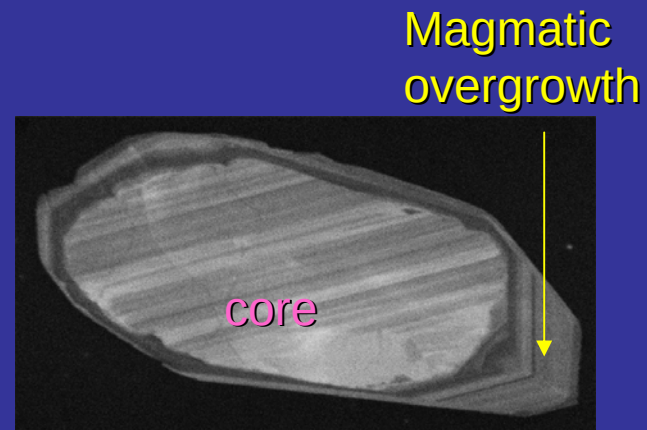


Internal structure of zircon

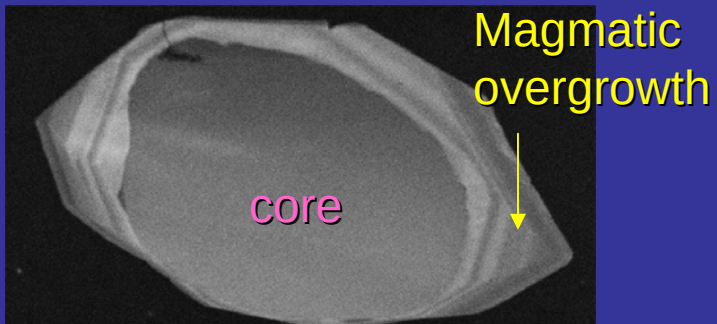
- recording the geological history



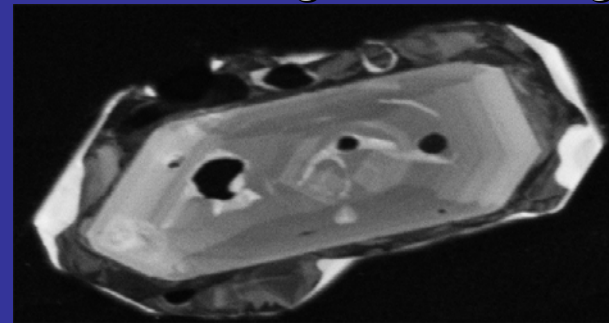
Simple magmatic zoning



Magmatic zircon with
core of magmatic zoning



Magmatic zircon with
core of recrystallization



Strong recrystallization

锆石内部结果分析方法

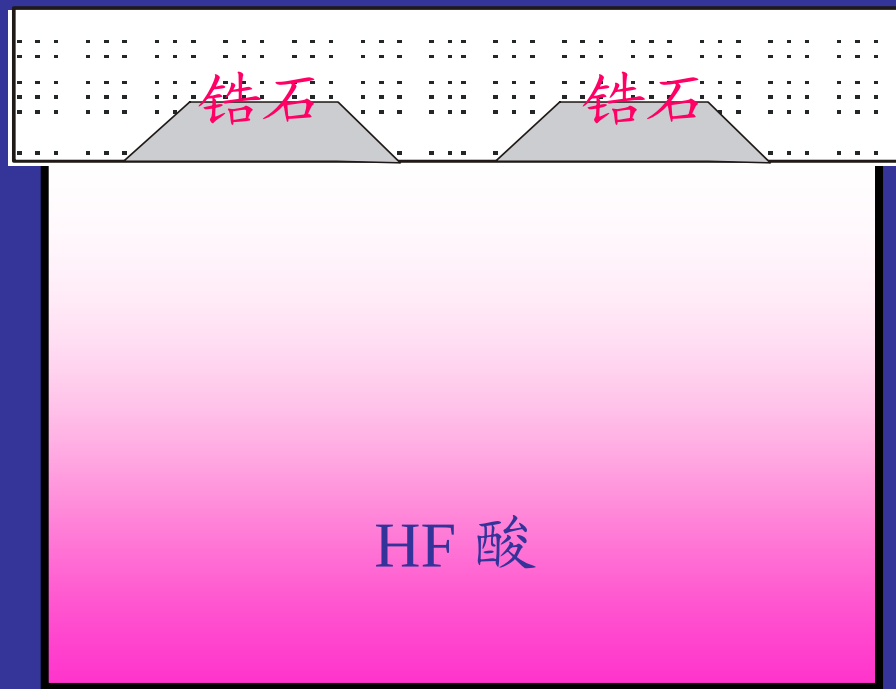
HF酸蚀刻法

背散射电子图像

阴极发光电子图像

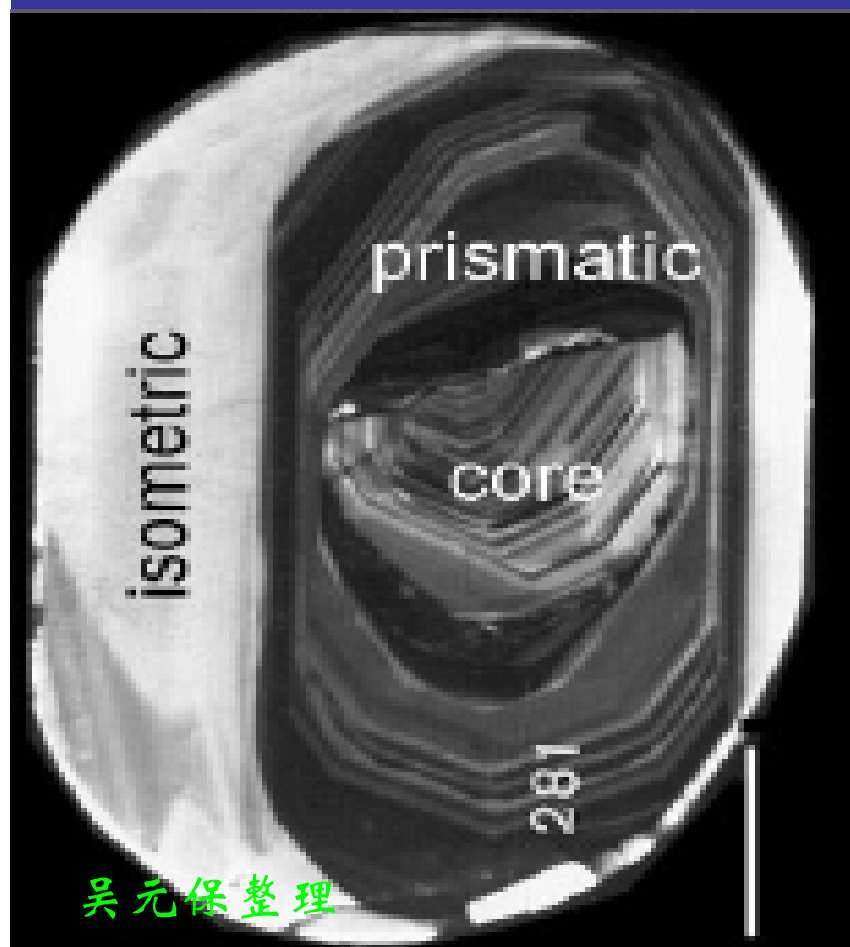
氢氟酸(HF)蚀刻法

锆石抗HF酸腐蚀能力不同



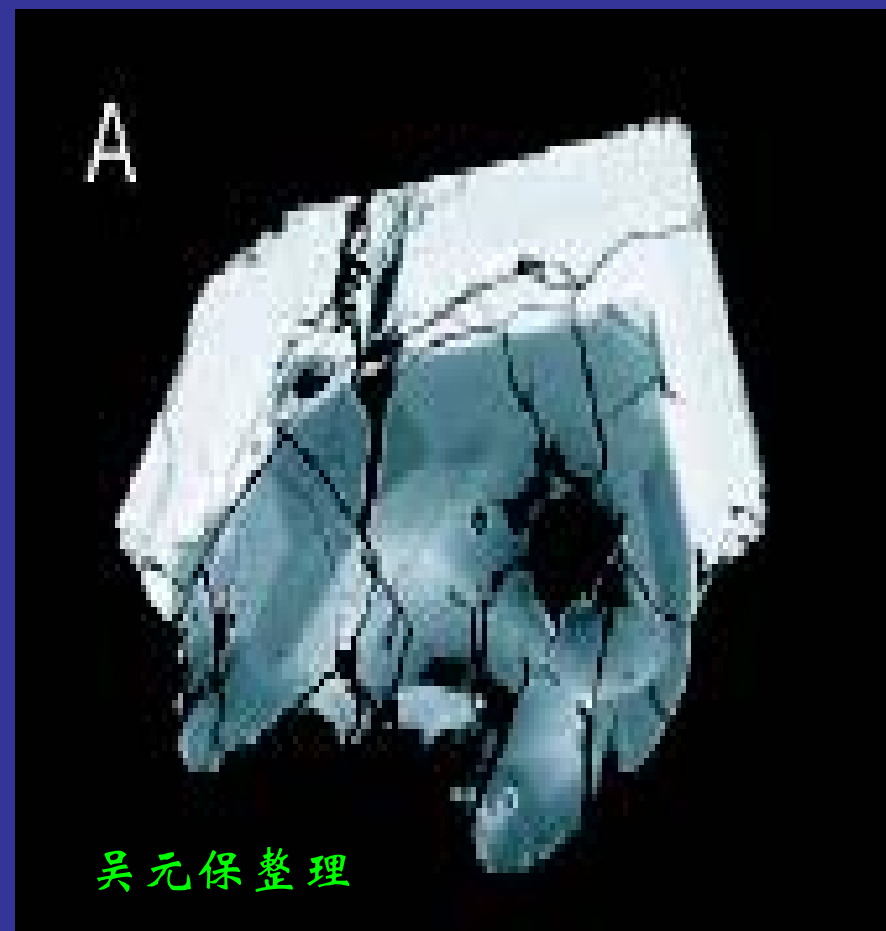
阴极发光图像 (CL)

微量元素含量和晶体缺陷
可以清楚显示内部结构



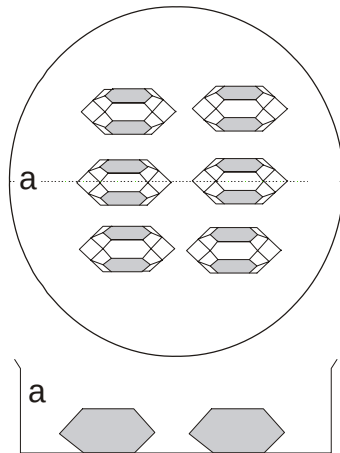
背散射电子图像

锆石表面平均分子量
表面特征清楚

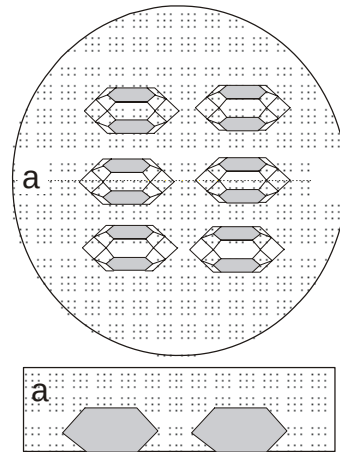


Cathodoluminescence

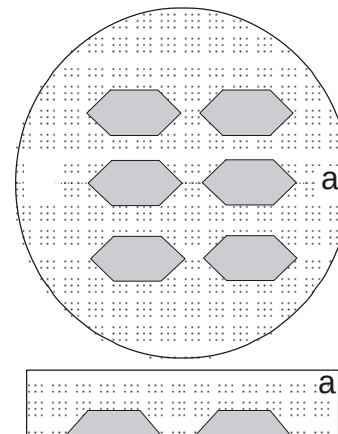
1) Set zircons on the bottom of a vessel



2) Input resin in the vessel

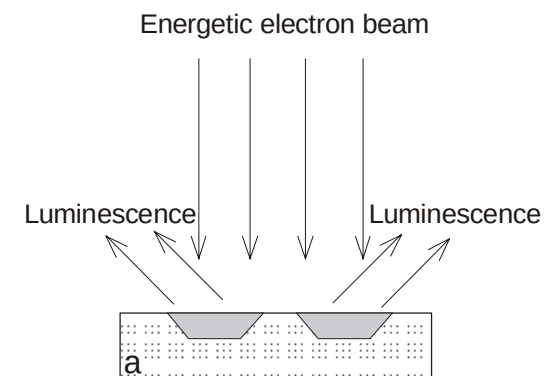


3) After polish



阴极发光

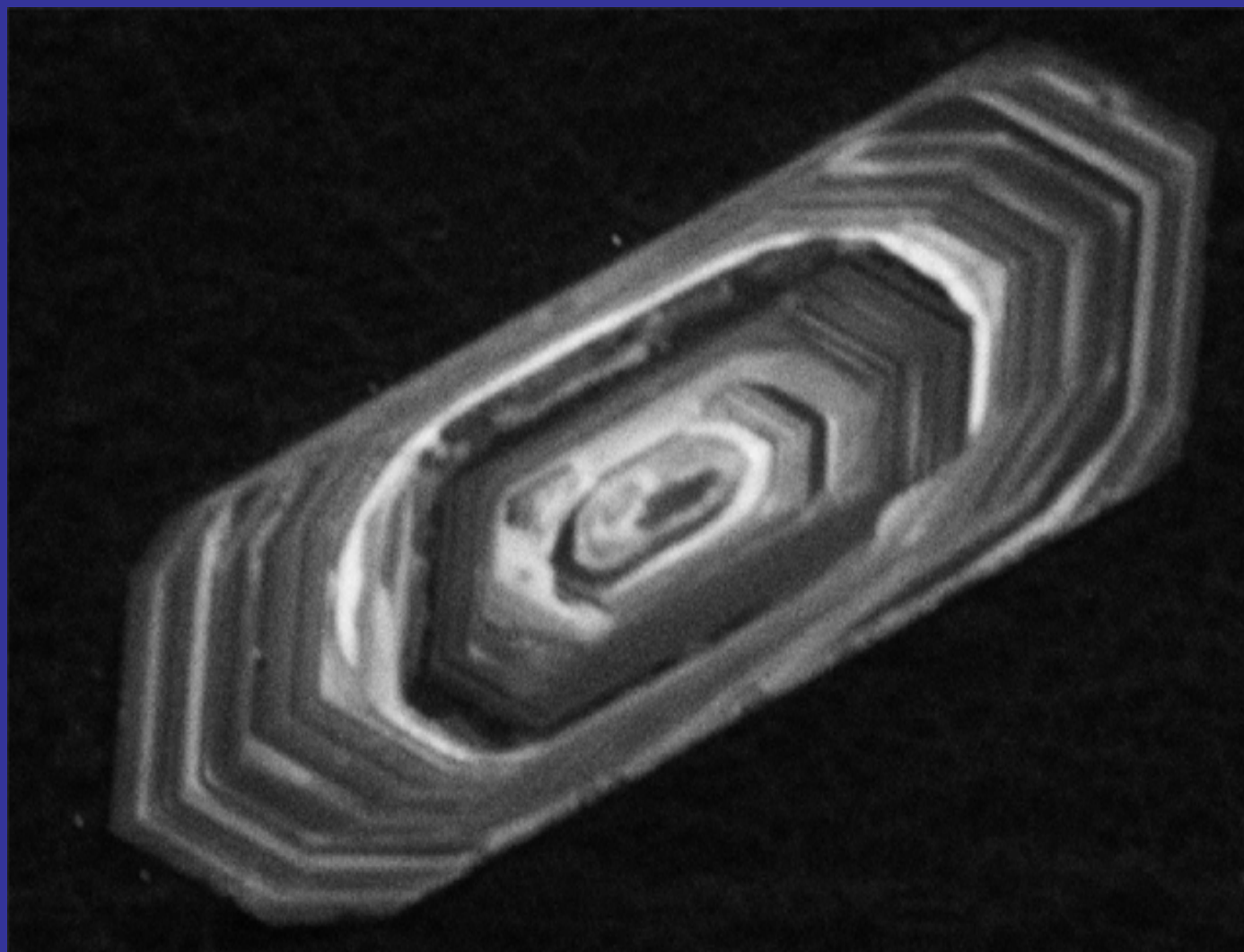
4) Cathodoluminescence analysis





Cameca 电子探针

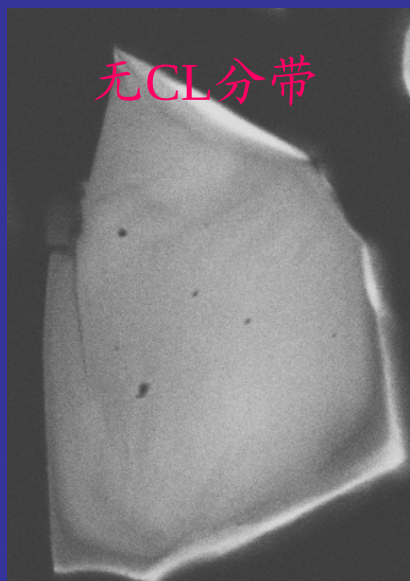
典型岩浆锆石阴极发光图像



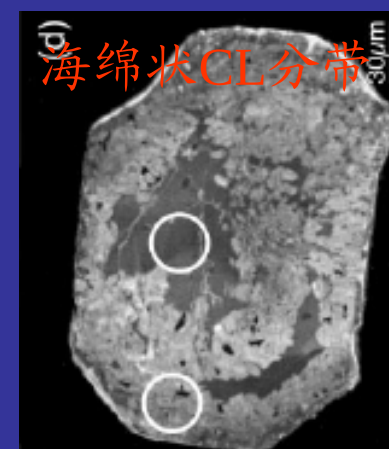
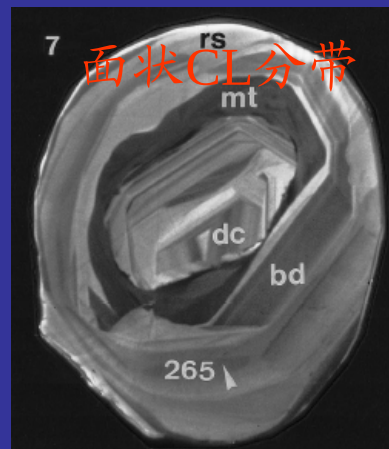
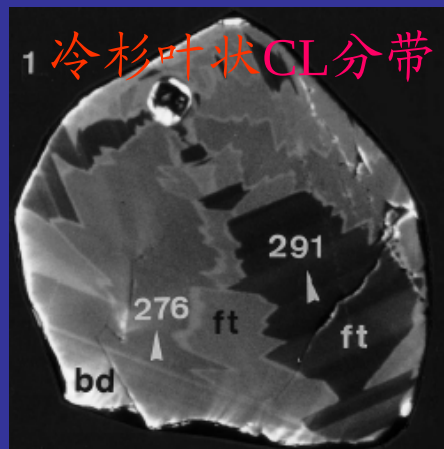
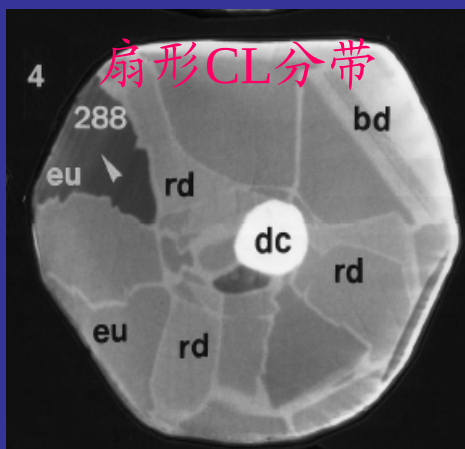
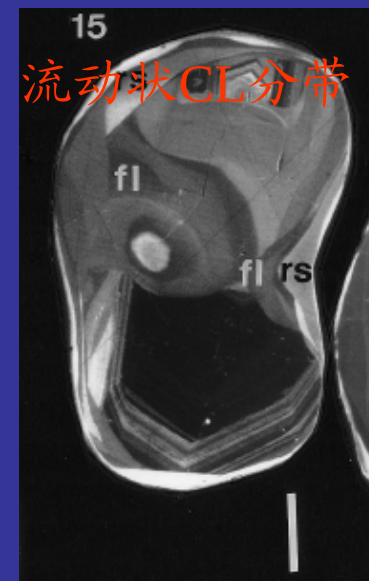
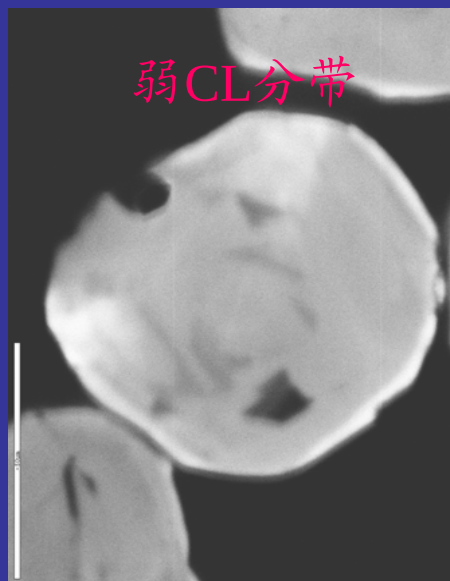
变质锆石CL内部结构 (吴元保整理)



无CL分带



弱CL分带



岩浆成因锆石

较高的Th、U含量和Th/U比值 ($\text{Th}/\text{U} > 0.4$)

分异结晶晚期岩浆锆石低Th/U比值 (< 0.1)

变质重结晶锆石

Th和U含量及Th/U比值变化范围较大

变质成因锆石

较低的Th、U含量和Th/U比值 ($\text{Th}/\text{U} < 0.1$)

谢谢