第三届“非传统稳定同位素地球化学”暑期学校

第三讲：

LA-MC-ICPMS在同位素分析的应用

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提　纲

- 非传统稳定同位素和原位微区分析技术
- 同位素原位微区分析的要点
- Cu同位素LA-MC-ICPMS微区分析
- Fe同位素LA-MC-ICPMS微区分析
- 小结

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同位素分析技术

1. 整体 (bulk) 分析

将样品消解经离子交换分离出同位素，再用热电离质谱（TIMS）或多接收-等离子体质谱（MC-ICP-MS）技术测定其同位素组成

2. 微区 (in situ) 分析

用微钻取样/离子探针（SIMS）/激光剥蚀-等离子质谱（LA-MC-ICPMS）对固体样品在几十微米空间尺度上直接测定同位素组成

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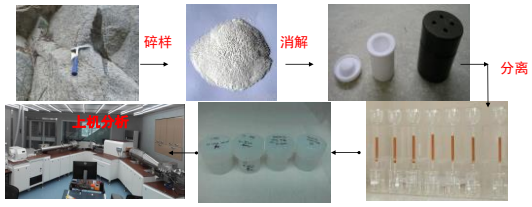
同位素分析技术

1. 整体 (bulk) 分析: TIMS or MC-ICP-MS



- **不能混入空白，仪器选择、基体效应、分馏校正等等**
- **MC-ICP-MS OR TIMS**
- **合适的样品信号、仪器参数的调节、基质影响以及标样测定等**

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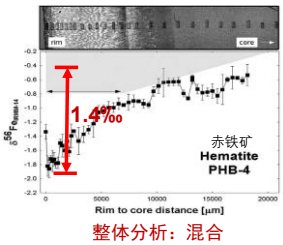
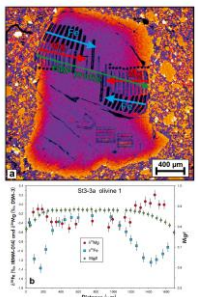
同位素分析技术

2. 微区原位（in situ）分析　Why in situ ?



整体分析：混合

I. Horn et al. (2006)



M Oeser et al., 2014, GGR

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同位素分析技术

微区原位（in situ）分析技术手段（SIMS & LA）

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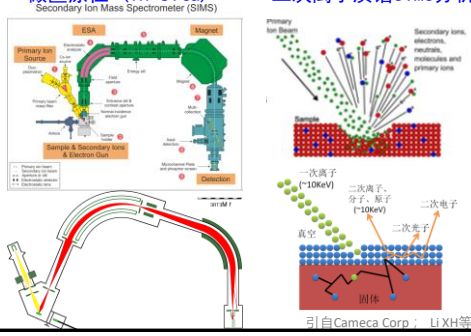
同位素分析技术

• 微区原位（in situ）—— 二次离子质谱SIMS分析



引自Cameca Corp； Li XH等

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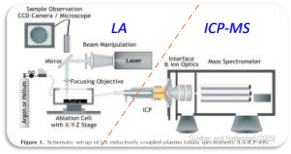
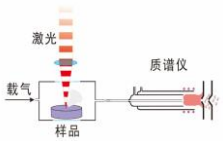
同位素分析技术

• 微区原位（in situ）—— LA-Q/SF/MC-ICPMS分析





激光剥蚀等离子质谱：LA-ICP-MS（1985 — ）

***LA-ICP-MS:* *L*aser *A*blation *I*nductively *C*oupled *P*lasma *M*ass *S*pectrometry**

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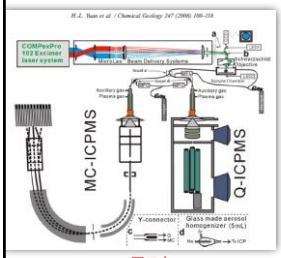
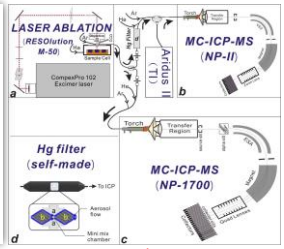
同位素分析技术

微区原位（in situ）—— LA-Q/SF/MC-ICPMS分析



一石三鸟

U-Pb age + REE + Hf isotope



一石二鸟

S isotope + Pb isotope

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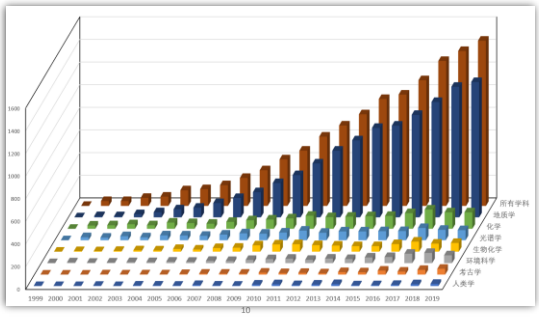
LA-ICP-MS在不同学科的应用情况



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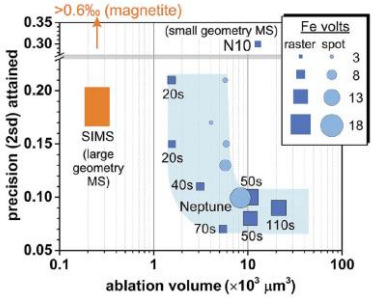
过去20年间，各学科利用LA-ICP-MS发表的文章，数据来源于ISI Web of Science

同位素分析技术

Fe同位素：SIMS *vs.* LA-MC-ICPMS



X-Y Zheng *et al.*,JAAS,2018

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LA-MC-ICPMS位素分析的难点

- 仪器质量歧视效应 mass bias
- 基体效应matrix effect:

  质谱干扰（同质异位素、双电荷、多原子离子）
  Spectral （non-mass dependent）
  非质谱干扰（不同矿物基体元素）
  Non-Spectral （mass-dependent）

- 激光剥蚀和传输过程的同位素分馏效应
  Laser induced mass fractionation
- 缺少微区分析同位素标样
  Well-characterized standard

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LA-MC-ICPMS位素分析的难点

- 仪器质量歧视效应　　利用SSB法等校正
- 基体效应：
  - 质谱干扰　　纯化和高分辨率
  - 非质谱干扰　　剥蚀条件参数、数算
- 激光剥蚀和传输过程的分馏　基体匹配
- 缺少微区分析同位素标样　研制

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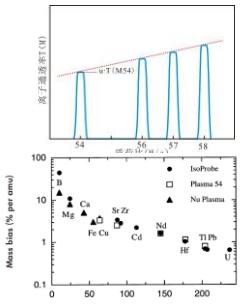
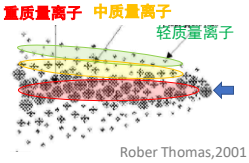
同位素分析的难点-质量歧视效应





Rober Thomas,2001

M.Rehkämper,GGR,2001

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同位素分析的难点-质量歧视效应

质量歧视效应mass bias的解决办法：

- 双稀释剂法Double spike (DS)
- 元素加入法Element doping
- 标准-样品交叉法Standard－Sample Bracketing technique (SSB)

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同位素分析的难点-质量歧视效应

质量歧视效应mass bias的校正公式：

SSB:

$$r_{corr} = R_{std} \times \frac{r_{meas}}{\sqrt{(r_{std})_1 \times (r_{std})_2}} \quad (1)$$

Power law:

$$\alpha = \left(\frac{R_{true}}{r_{meas}}\right)^{1/\Delta M} - 1 \quad (2)$$

$$r_{corr} = r_{meas}(1+\alpha)^{\Delta m} \quad (3)$$

Exponential law:

$$\beta = Ln(R_{true}/r_{meas})/Ln(M_i/M_k) \quad (4)$$

$$r_{corr} = r_{meas}(M_i/M_k)^{\beta} \quad (5)$$

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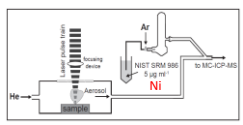
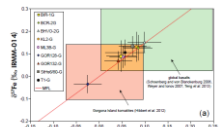
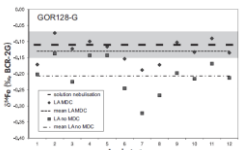
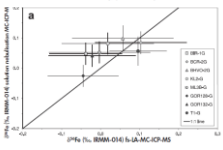
同位素分析的难点-质量歧视效应

Fe同位素Fs-LA , Ni doping









Martin Oeser, 2014, GGR

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同位素分析的难点-基体效应
质谱干扰—Fe同位素

Isobaric (spectral) interferences for Iron isotopes.

Isotope	Abundance (%)	Mass	interference	Interference mass	ΔM	R=M/ΔM
$^{53}Cr^+$	9.5006	52.94065	$[^{40}Ar^{13}C]^+$	52.96573	0.02508	2111
$^{54}Cr^+$	2.3647	53.93888	$[^{40}Ar^{14}N]^+$	53.96545	0.02657	2030
$^{54}Fe^+$	5.84	53.93961	$[^{40}Ar^{14}N]^+$	53.96545	0.02584	2087
			$^{54}Cr^+$	53.93888	0.00073	73804
			$[^{40}Ca^{14}N]^+$	53.96566	0.02605	2071
			$[^{42}Ca^{13}C]^+$	53.95862	0.01901	2837
			$[^{37}Al^{17}Al]^+$	53.96308	0.02347	2298
$^{56}Fe^+$	91.76	55.93494	$[^{40}Ar^{16}O]^+$	55.95729	0.02235	2503
			$[^{40}Ca^{16}O]^+$	55.95750	0.02256	2479
			$[^{54}Cr^{2}H]^+$	55.95386	0.01892	2956
$^{57}Fe^+$	2.12	56.93540	$[^{40}Ar^{16}O^1H]^+$	56.96512	0.02972	1916
			$[^{40}Ar^{17}O]^+$	56.96151	0.02611	2181
$^{58}Fe^+$	0.25	57.93328	$^{58}Ni^+$	57.93535	0.00207	27967
			$[^{40}Ar^{18}O]^+$	57.96154	0.02826	2050

- 同质异位素干扰：如$^{54}Cr^+$, $^{58}Ni^+$ 等
- 多原子离子干扰：如$^{40}Ar^{16}O^+$, $^{40}Ar^{14}N^+$ 等
- 双电荷离子干扰：如$^{108}Cd^{++}$, $^{112}Cd^{++}$, $^{112}Sn^{++}$ 等

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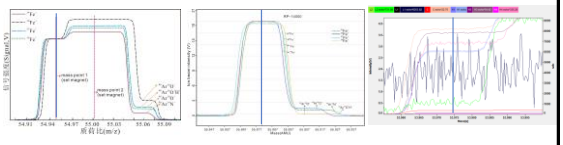
同位素分析的难点–基体效应
质谱干扰—Fe同位素

RP=8000-10000　　RP=20000　　RP=8000-10000



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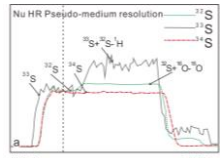
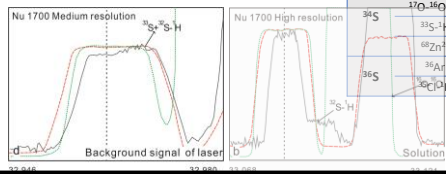
同位素分析的难点–基体效应
质谱干扰—S同位素



	干扰	m/Δm
^{32}S	^{16}O-^{16}O	1801
	$^{64}Zn^{2+}$	-4562
	^{15}N-^{16}O-^{1}H	1040
^{33}S	^{17}O-^{16}O	1461
	^{16}O-^{16}O-^{1}H	1260
	^{32}S-^{1}H	3907
	$^{66}Zn^{2+}$	-3905
^{34}S	^{18}O-^{16}O	1297
	^{17}O-^{16}O-^{1}H	1000
	^{33}S-^{1}H	2977
	$^{68}Zn^{2+}$	-6238
^{36}S	^{36}Ar	76526
	^{35}Cl-^{1}H	3747



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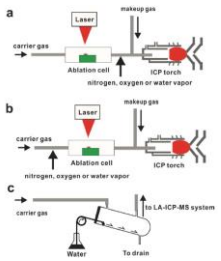
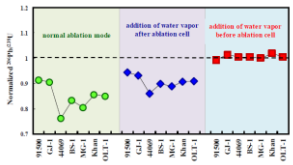
同位素分析的难点–基体效应
非质谱干扰　复杂的矿物成分



副矿物U-Pb同位素定年



T Luo *et al.*,AC,2018

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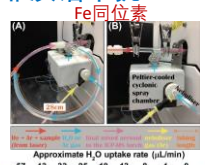
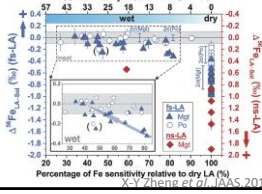
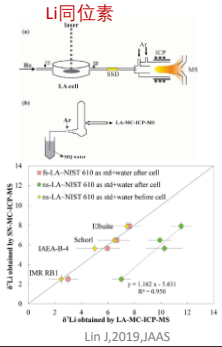
同位素分析的难点–基体效应
非质谱干扰

Fe同位素　　Li同位素





X-Y Zheng *et al.*, JAAS 2018



Lin J,2019,JAAS

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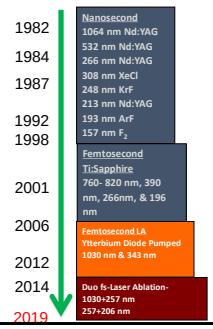
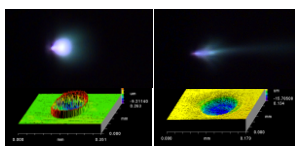
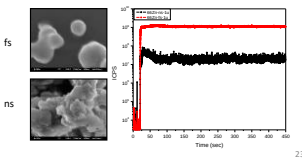
同位素分析的难点–激光分馏效应

激光剥蚀系统的发展







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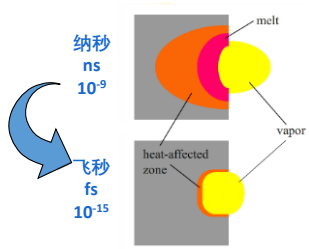
激光脉冲宽度：纳秒 → 飞秒

激光剥蚀系统发展的趋势（脉宽）：**更短脉宽**



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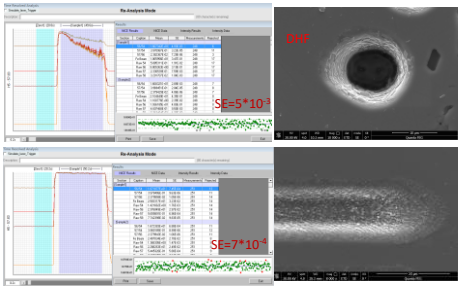
同位素分析的难点–激光分馏效应



不同矿物类型、复杂的变化的矿物成分、激光剥蚀和气溶胶传输过程、ICP电离过程综合导致了复杂的同位素分馏行为

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同位素分析的难点–基体效应

实测数据包含了质量歧视、基体效应和激光诱导分馏效应的叠加

- 仪器分析参数、条件
- 标准样品（基体匹配）

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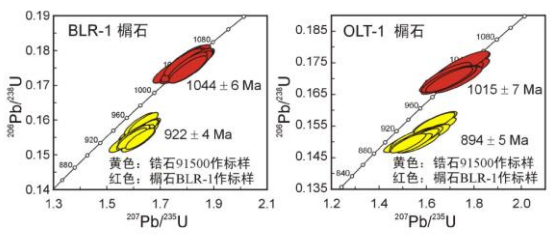
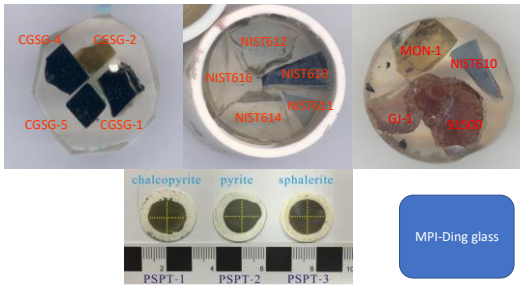
以锆石和榍石为外标，测定榍石的U-Pb年龄，单点分析，存在着基体效应



孙金凤等，科学通报，2012

同位素分析的难点–参考物质缺乏

目前仅有少量同位素具有个别矿物的同位素微区参考物质



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标准样品

- NIST玻璃 (NIST 610, 612, 614)
- USGS玻璃 (GSE-1G, GSD-1G, GSC-1G)
- USGS 玻璃 (BCR-2G, BHVO-2G, BIR-1G)
- MPI-DING玻璃 (SiO_2 = 45 -75%)
- CGSG玻璃(SiO_2 = 53 - 64%)
- USGS碳酸盐 (MACS-3、GP-4)、磷酸盐 (MAPS-4、 MAPS-5) 和硫化物压片 (MASS-1)
- 其他玻璃（如Cpx、榍石、磷酸盐、BAM-S005-A and BAM-S005-B)
- 各实验室研制的标准样品

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利用LA-ICP-MS分析地质样品要点

1. 分析前的准备工作
2. 选择合适的外标样品
3. 不同内标元素对分析结果的影响
4. 不同校正方案对分析结果的影响
5. 利用LA-ICP-MS分析主要地质样品

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第一步：分析前的准备工作

- 全岩整体分析
- 矿物单点微区分析
- 深度分析/剖面分析
- 熔体包裹体
- 流体包裹体
- ……

- 制备样品（压饼、熔片、抛光等）
- 岩相学研究
- 标记分析点位
- 测盐度（流体包裹体）

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第二步：制定分析方案

- 制定校正方案（内标法/无内标法、外标）
- 基体扣除和定量化方案（包裹体）
- 激光剥蚀条件（束斑、能量密度、频率、线扫描速度等）
- 选择分析同位素
- ICP-MS数据采集参数（包裹体需要长时间）

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同位素原位微区分析

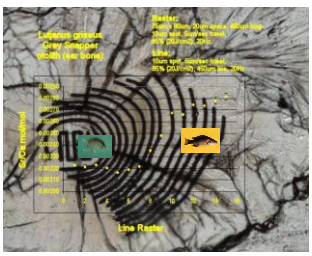
Journal of Asian Earth Sciences，2018，2019

第三步：选择合适的分析方式

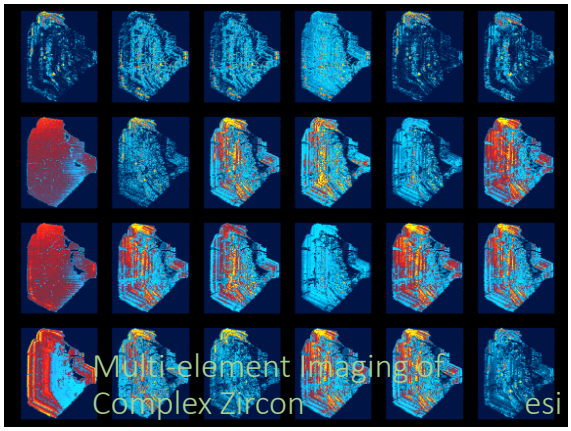
- 单点剥蚀
- 线扫描
- 面扫描
- 3D扫描

Simon Jackson

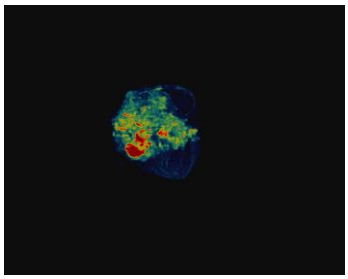
FISH OTOLITH ANALYSIS



Simon Jackson



HDIP Software



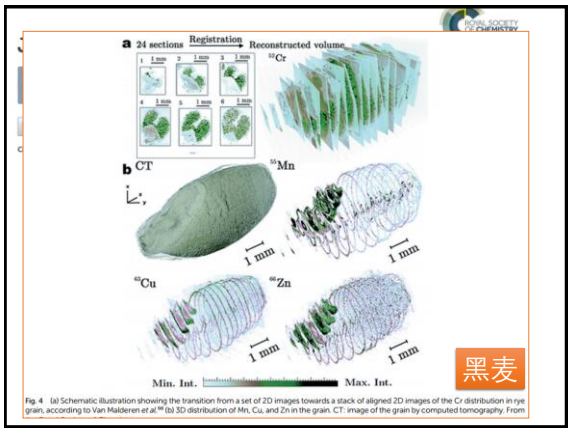


Fig. 4 (a) Schematic illustration showing the transition from a set of 2D images towards a stack of aligned 2D images of the Cr distribution in rye grain, according to Van Malderen *et al.*[66] (b) 3D distribution of Mn, Cu, and Zn in the grain. CT: image of the grain by computed tomography. From

第四步：数据处理

- **ICPMSDataCal**
  - 中国地质大学（武汉）刘勇胜教授
- **Iolite**
  - Melbourne University
- **GLITTER**
  - Macquarie University

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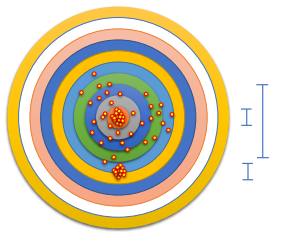
精度 vs 准确度



对比与展望

	ID-TIMS	SIMS	LA-(MC)-ICPMS	LA-ICPMS
精度	←	←	←	←
微观信息	No	←	←	←
基体效应	No	矿物结构 化学成分	—	矿物结构
效率	→	→	→	→

根据科学目的和样品具体情况选择合适的分析方法

例 1：

Cu同位素微区分析

Cu同位素简介

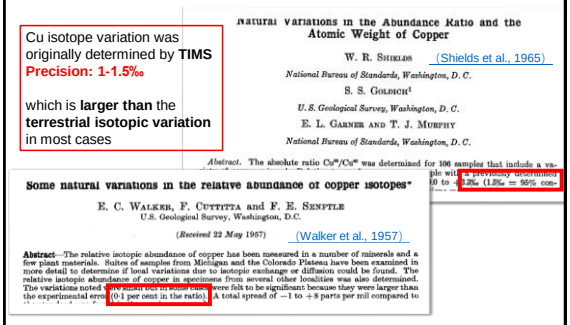
- ✓ 2 stable isotope:

^{63}Cu 62.92960 69.17%　　^{65}Cu 64.92779 30.83%

- ✓ Primary standard: NIST 976 (美国国家标准技术研究所，纯铜)
  $^{65}Cu/^{63}Cu$=0.4456±0.0004 (Shields et al., 1964)
- ✓ Other standard: IRMM, GSB Cu, NIST SRM 3114, NWU-CuA, NWU-CuB
- ✓ 表达方式：$\delta^{65}Cu = \left(\left(\frac{^{65}Cu/^{63}Cu_{sample}}{^{65}Cu/^{63}Cu_{NIST976}}\right) - 1\right) \times 1000$

Cu isotope variation was originally determined by **TIMS**
Precision: 1-1.5‰

which is **larger than** the **terrestrial isotopic variation** in most cases



Natural Variations in the Abundance Ratio and the Atomic Weight of Copper

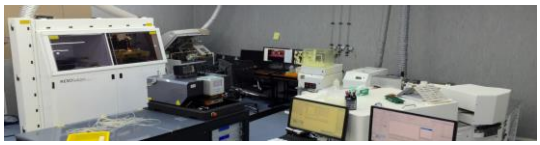
W. R. Shields (Shields et al., 1965)
National Bureau of Standards, Washington, D. C.
S. S. Goldich[1]
U.S. Geological Survey, Washington, D. C.
E. L. Garner and T. J. Murphy
National Bureau of Standards, Washington, D. C.

Abstract. The absolute ratio Cu^{65}/Cu^{63} was determined for 100 samples that include a va- ... a previously unreported ... 0.2‰ (1.8‰ = 95% con-

Some natural variations in the relative abundance of copper isotopes*

E. C. Walker, F. Cuttitta and F. E. Senftle
U.S. Geological Survey, Washington, D.C.
(Received 22 May 1957) (Walker et al., 1957)

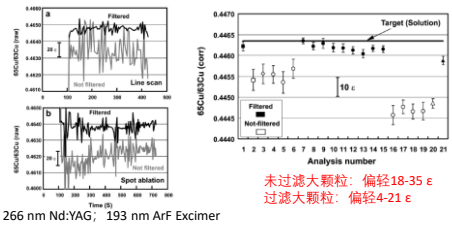
Abstract—The relative isotopic abundance of copper has been measured in a number of minerals and a few plant materials. Suites of samples from Michigan and the Colorado Plateau have been examined in more detail to determine if local variations due to isotopic exchange or diffusion could be found. The relative isotopic abundance of copper in specimens from several other localities was also determined. The variations noted ... (0·1 per cent in the ratio). A total spread of −1 to +8 parts per mil compared to



✓**MC-ICP-MS**
✓优点：
目前精度最高
✓缺点：
化学分离流程繁琐，耗时，样品容易互相污染；
混合数据。

✓**LA-MC-ICP-MS**
✓优点：
原位微区分析。
✓缺点：
基体效应；
设备要求高。

ns LA-MC-ICP-MS

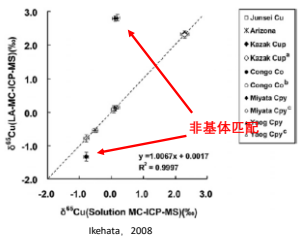


266 nm Nd:YAG，193 nm ArF Excimer
过滤剥蚀气溶胶中的大颗粒

未过滤大颗粒：偏轻18-35 ε
过滤大颗粒：偏轻4-21 ε

Jackson,2003

fs LA-MC-ICP-MS

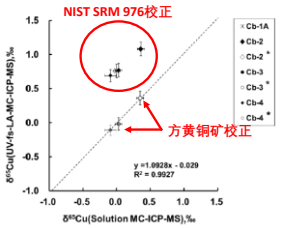


Ikehata，2008

- NIR fsLA,780nm
- 标样NIST SRM 976可以矫正自然铜，赤铜矿，对于辉铜矿，黄铜矿基体效应明显
- 精度（2SD）：0.08-0.14‰
- 矫正方法：SSB

fs LA-MC-ICP-MS

- **UV fsLA**,260nm
- 标样NIST SRM 976矫正方黄铜矿基体效应明显
- 使用实验室内部方黄铜矿标样校正，精度（2SD）0.1‰
- 矫正方法：SSB



Ikehata，2013

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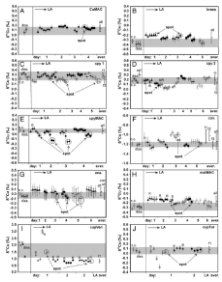
fs LA-MC-ICP-MS

- **UV fsLA**, 194nm
- 用纯铜标样NIST SRM 976矫正纯铜，黄铜，黄铜矿，赤铜矿，砷硫铜矿，铜蓝，孔雀石，并认为可以实现非基体匹配的校正
- 精度（2SD）：0.08‰
- 矫正方法：SSB + Ni (internal standard)



Lazarov，2015

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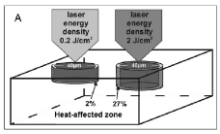
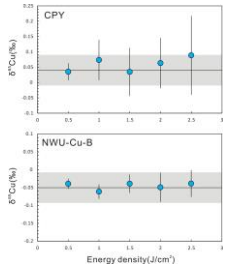
Effect of Fluence



Lazarov，2015

- 前人研究认为更高的能量密度会影响$\delta^{65}Cu$的测定
- 能量从0.5-2.5J/cm²，黄铜矿和纯铜的$\delta^{65}Cu$的值都在0.05‰的误差范围内，但精度（2SD）变差



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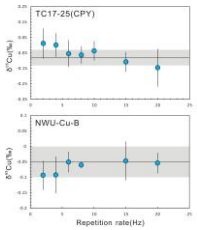
Effect of Repetition Rate

- 频率对于$\delta^{65}Cu$影响明显
- 黄铜矿随着频率增加，$^{65}Cu/^{63}Cu$增加，$\delta^{65}Cu$趋向更轻
- 纯铜受到频率的影响较小，但是当频率≤4Hz时，$\delta^{65}Cu$趋向更轻
- 最佳的频率在6-15Hz之间



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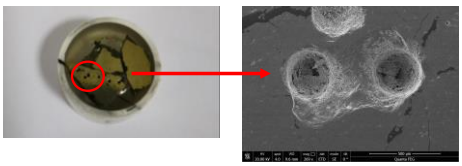
Matrix effect



- 微钻在样品表面钻取样品溶解，利用MC-ICP-MS测定溶液值
- 在钻孔附近利用激光剥蚀测定$\delta^{65}Cu$
- 标样：实验室内部标样TC17-25（黄铜矿）

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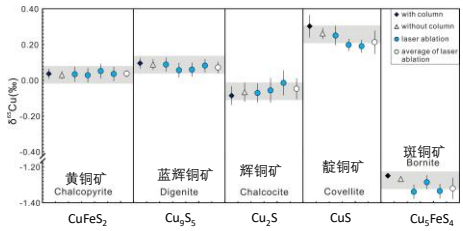

用黄铜矿TC17-25校正基体相同或相似的样品，可以获得0.05‰误差范围内的值

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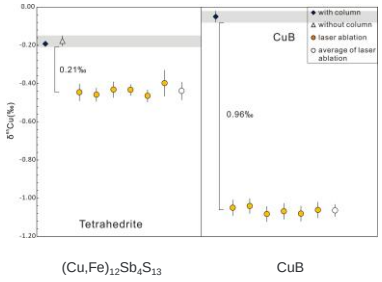

对于基体明显不同的样品，利用206nm飞秒激光剥蚀分析获得的值与MC-ICP-MS溶液值相差较大。

表现为明显的基体效应。

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小结

- 较低的能量密度（0.5–2.5 J·cm^{-2}）
- 剥蚀频率（6-15Hz）
- 较高的空间分辨率（10μm，10×50μm ）
- 精密度和准确度（优于0.10‰-0.05%, 2SD）

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例 2：

Fe 同位素微区分析

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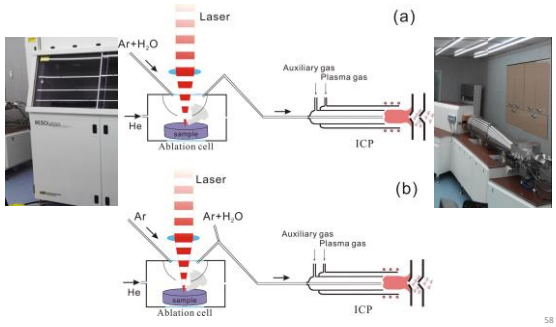
Fe同位素微区分析实验方法建立



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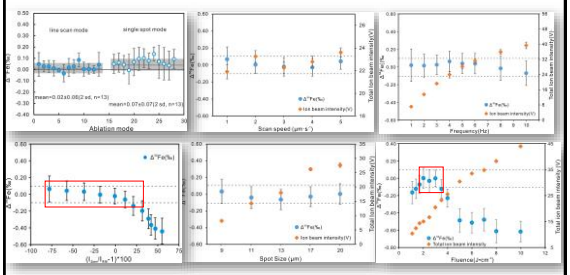
激光斑束、频率和能量密度等的影响



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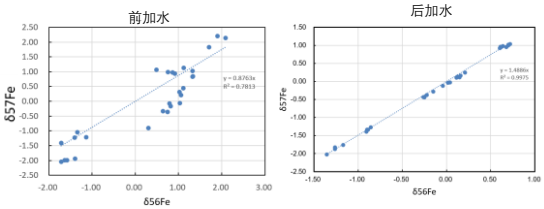
水蒸气对Fe同位素的影响



水蒸气的加入对Fe同位素测试的影响：以AA018黄铁矿为标样，剥蚀池前面和后面加水

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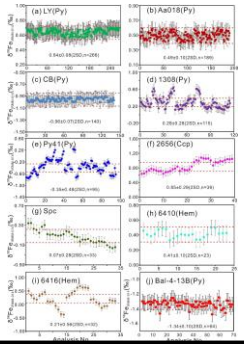
均一性检验：不同矿物中Fe同位素组成



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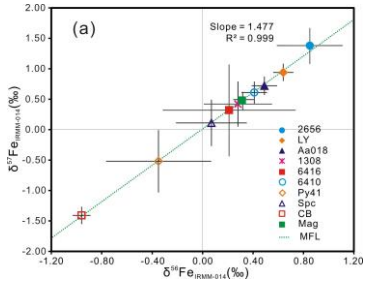
Fe同位素质量分馏线



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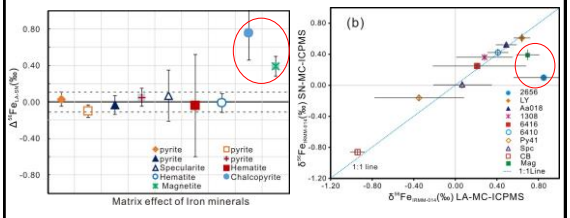
基体效应和分析准确度



不同矿物之间存在基体效应，相同矿物基体匹配可获得较高精度（优于0.10‰，2SD）

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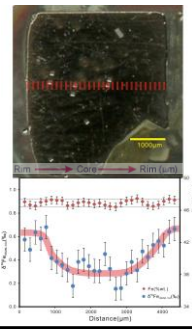
黄铁矿剖面扫描



黄铁矿晶体颗粒4.5mm
从中心到边部，Fe含量基本没有变化，但Fe同位素组成变化较大，（0.3—0.7‰）。

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小 结

- 较低的能量密度(1.5–3.5 J·cm^{-2}),
- 线扫描或单点模式
- 水蒸气可有效抑制基体效应
- 较高的空间分辨率（17μm，13×60μm ）
- 精密度和准确度（优于0.10‰，2SD）

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合适的标准样品
合适的仪器参数
合适的校正方法

→ 分析数据可靠

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一个优秀的实验室：

- 合理的团队
- 规范的管理
- 稳定的支持
- 化学与仪器

→

- 高质量数据
- 优秀的成果

公共服务　交流与合作

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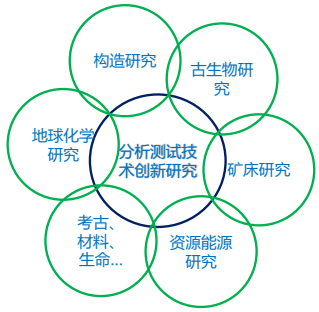

学科交叉、融合创新

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Table 3 Sr, Nd, and Hf isotopic ratios determined for the CRMs using the high-pressure PTFE bomb method and MC-ICP-MS

CRMs	$^{87}Sr/^{86}Sr$ (±2SE)	$^{145}Nd/^{144}Nd$ (±2SE)	$^{143}Nd/^{144}Nd$ (±2SE)	$^{176}Hf/^{177}Hf$ (±2SE)
GSP-2	0.765076 (9)	0.348399 (4)	0.511377 (5)	0.281940 (6)
	0.765084 (9)	0.348398 (6)	0.511362 (5)	0.281948 (7)
	0.765097 (8)	0.348398 (6)	0.511377 (7)	0.281946 (6)
	0.765147 (7)	0.348394 (4)	0.511389 (5)	0.281950 (6)
	0.765108 (9)	0.348384 (6)	0.511358 (7)	0.281946 (6)
	0.765145 (12)	0.348396 (8)	0.511363 (10)	0.281954 (5)
Mean (2SD)	**0.765109 ± 61**		**0.511373 ± 25**	**0.281948 ± 9**
GSR-1	0.738310 (9)	0.348398 (6)	0.512228 (6)	0.282520 (8)
	0.738314 (9)	0.348403 (8)	0.512223 (5)	0.282514 (7)
	0.738352 (14)	0.348403 (6)	0.512230 (6)	0.282525 (6)
	0.738289 (13)	0.348397 (8)	0.512220 (6)	0.282524 (6)
	0.738370 (13)	0.348394 (8)	0.512215 (5)	0.282518 (7)
	0.738340 (14)	0.348400 (9)	0.512221 (6)	0.282528 (6)
Mean (2SD)	**0.738329 ± 60**		**0.512223 ± 11**	**0.282522 ± 10**
QLO-1	0.703889 (8)	0.348388 (8)	0.512853 (9)	0.283045 (6)
	0.703887 (9)	0.348386 (4)	0.512853 (9)	0.283044 (7)
	0.703889 (9)	0.348392 (6)	0.512854 (8)	0.283051 (6)
	0.703892 (7)	0.348388 (8)	0.512856 (9)	0.283045 (5)
	0.703901 (9)	0.348403 (8)	0.512842 (8)	0.283055 (6)
	0.703891 (8)	0.348404 (8)	0.512849 (7)	0.283058 (5)
Mean (2SD)	**0.703891 ± 10**		**0.512851 ± 10**	**0.283050 ± 12**
AGV-2	0.703985 (6)	0.348389 (4)	0.512775 (7)	0.282977 (6)
	0.704006 (5)	0.348393 (6)	0.512782 (6)	0.282967 (7)
	0.703983 (9)	0.348403 (6)	0.512782 (9)	0.282971 (8)
	0.703989 (7)	0.348410 (6)	0.512788 (7)	0.282966 (9)
	0.704012 (11)	0.348416 (6)	0.512802 (9)	0.282973 (7)
	0.703984 (6)	0.348413 (8)	0.512790 (9)	0.282973 (7)
Mean (2SD)	**0.703993 ± 25**		**0.512787 ± 18**	**0.282971 ± 8**

有效数字取舍

standard deviation and standard error

- The standard deviation (often SD) is a measure of variability. When we calculate the standard deviation of a sample, we are using it as an estimate of the variability of the population from which the sample was drawn.
  （标准偏差：表示一组数值之间的离散程度）
- The standard error (often SE) of the sample mean depends on both the standard deviation and the sample size.
  （标准误差：表示样本统计量的标准偏差）

$$Standard\ error = \frac{standard\ deviation}{\sqrt{n}}$$

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内精度 和 外精度

Internal (within run) precision is calculated as:

$$\textbf{Relative Standard Error (1}\sigma\textbf{)} = \frac{\sqrt{\left(\left(X_n - \mathbb{X}\right)^2 / \left(n(n-1)\right)\right)}}{\mathbb{X}}$$

External (between run) precision is calculated as:

$$\textbf{Relative Standard Deviation (1}\sigma\textbf{)} = \frac{\sqrt{\left(\left(X_n - \mathbb{X}\right)^2 / \left(n-1\right)\right)}}{\mathbb{X}}$$

where X_n is the n^{th} value of parameter X
$\mathbb{X}$ is the average of all the data
n is the total number of data points present

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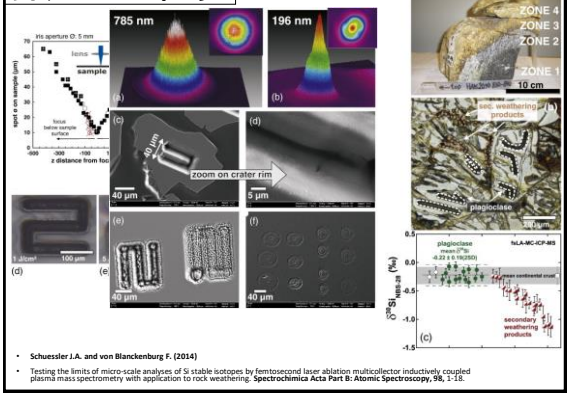
大陆动力学国家重点实验室激光和质谱仪

斜长石Si同位素



- **Schuessler J.A. and von Blanckenburg F. (2014)**
- Testing the limits of micro-scale analyses of Si stable isotopes by femtosecond laser ablation multicollector inductively coupled plasma mass spectrometry with application to rock weathering. **Spectrochimica Acta Part B: Atomic Spectroscopy, 98,** 1-18.