

第三届“非传统稳定同位素地球化学”暑期学校 (2020)

高温高压实验测定同位素分馏系数

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课程内容

1. 稳定同位素分馏理论简介
2. 高温高压实验方法介绍
3. 实验测定稳定同位素分馏系数原理
4. 实验研究实例

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稳定同位素

Periodic Table of the Elements

© www.elementsdatabase.com

H¹
Li³
Be⁴

Na¹¹
Mg¹²

K¹⁹
Ca²⁰
Sc²¹
Ti²²
V²³
Cr²⁴
Mn²⁵
Fe²⁶
Co²⁷
Ni²⁸
Cu²⁹
Zn³⁰

Rb³⁷
Sr³⁸
Y³⁹
Zr⁴⁰
Nb⁴¹
Mo⁴²
Tc⁴³
Ru⁴⁴
Rh⁴⁵
Pd⁴⁶
Ag⁴⁷
Cd⁴⁸

Cs⁵⁵
Ba⁵⁶
La⁵⁷
Hf⁷²
Ta⁷³
W⁷⁴
Re⁷⁵
Os⁷⁶
Ir⁷⁷
Pt⁷⁸
Au⁷⁹
Hg⁸⁰

Fr⁸⁷
Ra⁸⁸
Ac⁸⁹
Unq¹⁰⁴
Unp¹⁰⁵
Unh¹⁰⁶
Uns¹⁰⁷
Uno¹⁰⁸
Une¹⁰⁹
Unn¹¹⁰

B⁵
C⁶
N⁷
O⁸
F⁹

Al¹³
Si¹⁴
P¹⁵
S¹⁶
Cl¹⁷

Ga³¹
Ge³²
As³³
Se³⁴
Br³⁵

In⁴⁹
Sn⁵⁰
Sb⁵¹
Te⁵²
I⁵³

Tl⁸¹
Pb⁸²
Bi⁸³
Po⁸⁴
At⁸⁵

Ce⁵⁸
Pr⁵⁹
Nd⁶⁰
Pm⁶¹
Sm⁶²
Eu⁶³
Gd⁶⁴
Tb⁶⁵
Dy⁶⁶
Ho⁶⁷
Er⁶⁸
Tm⁶⁹
Yb⁷⁰
Lu⁷¹

Th⁹⁰
Pa⁹¹
U⁹²
Np⁹³
Pu⁹⁴
Am⁹⁵
Cm⁹⁶
Bk⁹⁷
Cf⁹⁸
Es⁹⁹
Fm¹⁰⁰
Md¹⁰¹
No¹⁰²
Lr¹⁰³

- 传统 (气体): H, C, N, O, S
- 非传统 (金属): Li, B, Mg, Si, Cl, K, Ca, Ti, V, Cr, Ni, Fe, Cu, Zn....

稳定同位素一些基本概念

同位素分馏：某元素的同位素以不同的比值分配到**两种物质或两相**中的现象，是同位素效应的表现。

同位素比值：某两个同位素丰度的比值，例如 $R = {}^{18}\text{O}/{}^{16}\text{O}$ ，分母一般为丰度**最大**的同位素。

同位素数据的表示： $\delta = (R_{\text{SAM}}/R_{\text{STD}} - 1) \times 1000\text{‰}$

- 热力学平衡分馏
- 动力学分馏
- 非质量相关分馏

稳定同位素分馏系数

实测 δ 值

$$\delta_A = (R_A/R_{STD} - 1) \times 1000\text{‰}$$

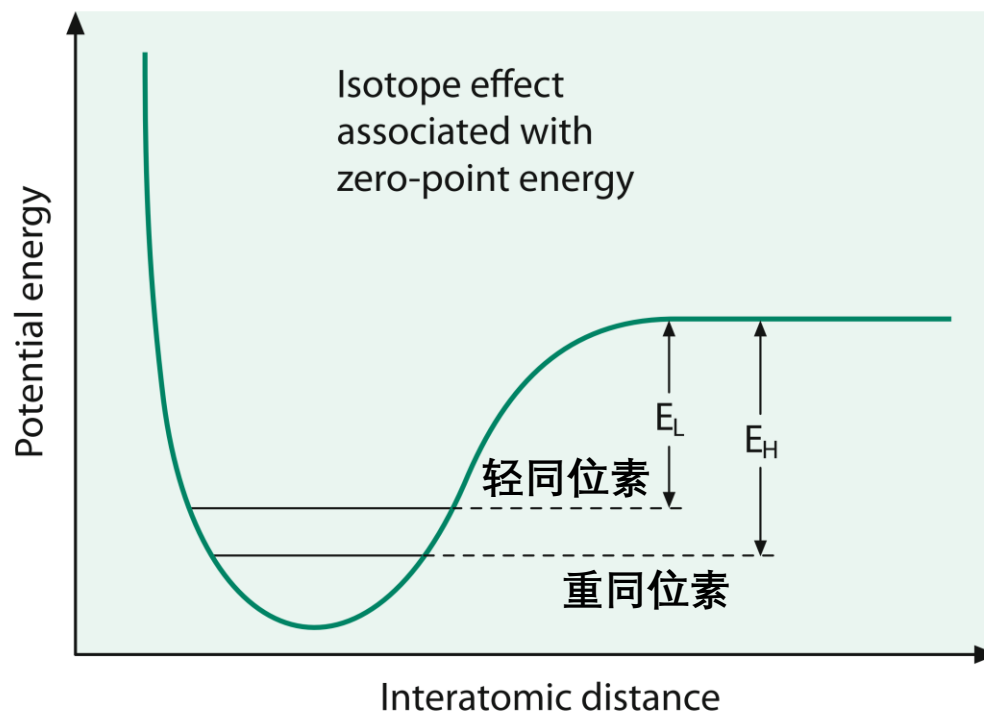
$$\delta_B = (R_B/R_{STD} - 1) \times 1000\text{‰}$$

- 同位素分馏值: $\Delta_{A-B} = \delta_A - \delta_B$,
- 分馏系数: $\alpha_{A-B} = R_A/R_B = (\delta_A + 1000)/(\delta_B + 1000)$
- $\alpha_{A-B} - 1 = (\delta_A - \delta_B)/(\delta_B + 1000) \approx (\delta_A - \delta_B)/1000$

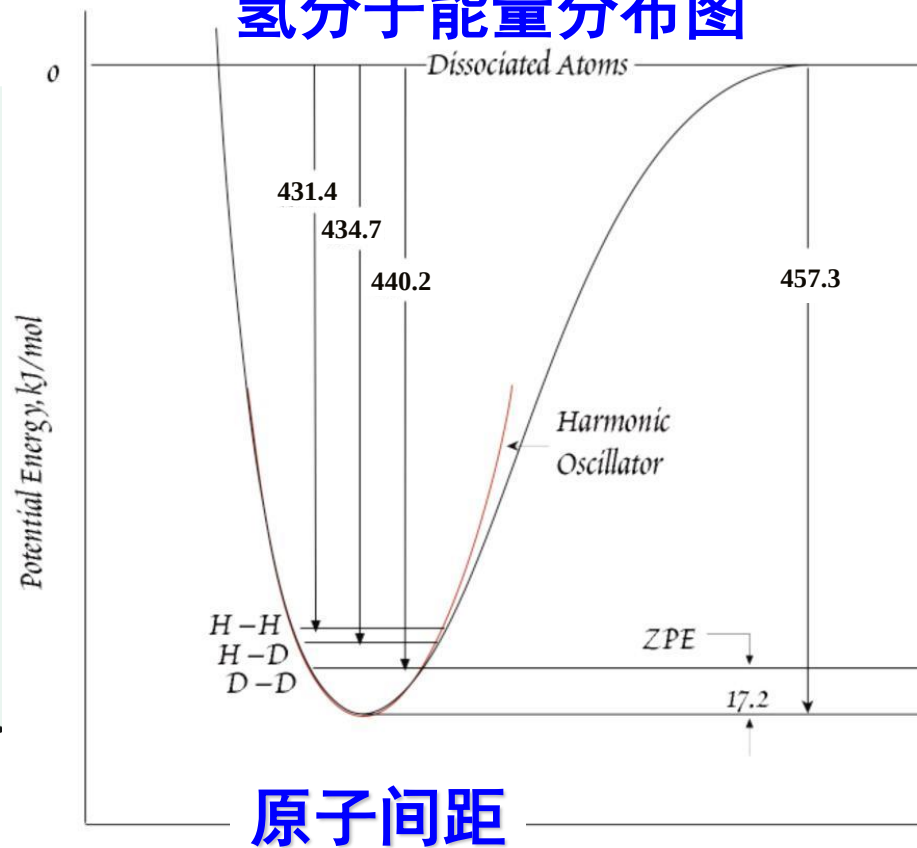
$$\alpha_{A-B} \approx 1$$

$$10^3 \ln \alpha_{A-B} \approx 10^3 (\alpha_{A-B} - 1) \approx \Delta_{A-B}$$

零点能理论



氢分子能量分布图



重质量数稳定同位素形成化学键较强分子，
较强化学键分子相对富集重质量数稳定同位素。

影响同位素平衡分馏的因素

□温度

$$10^3 \ln \alpha = A \times 10^6 / T^2 + B \times 10^3 / T + C$$

□压力

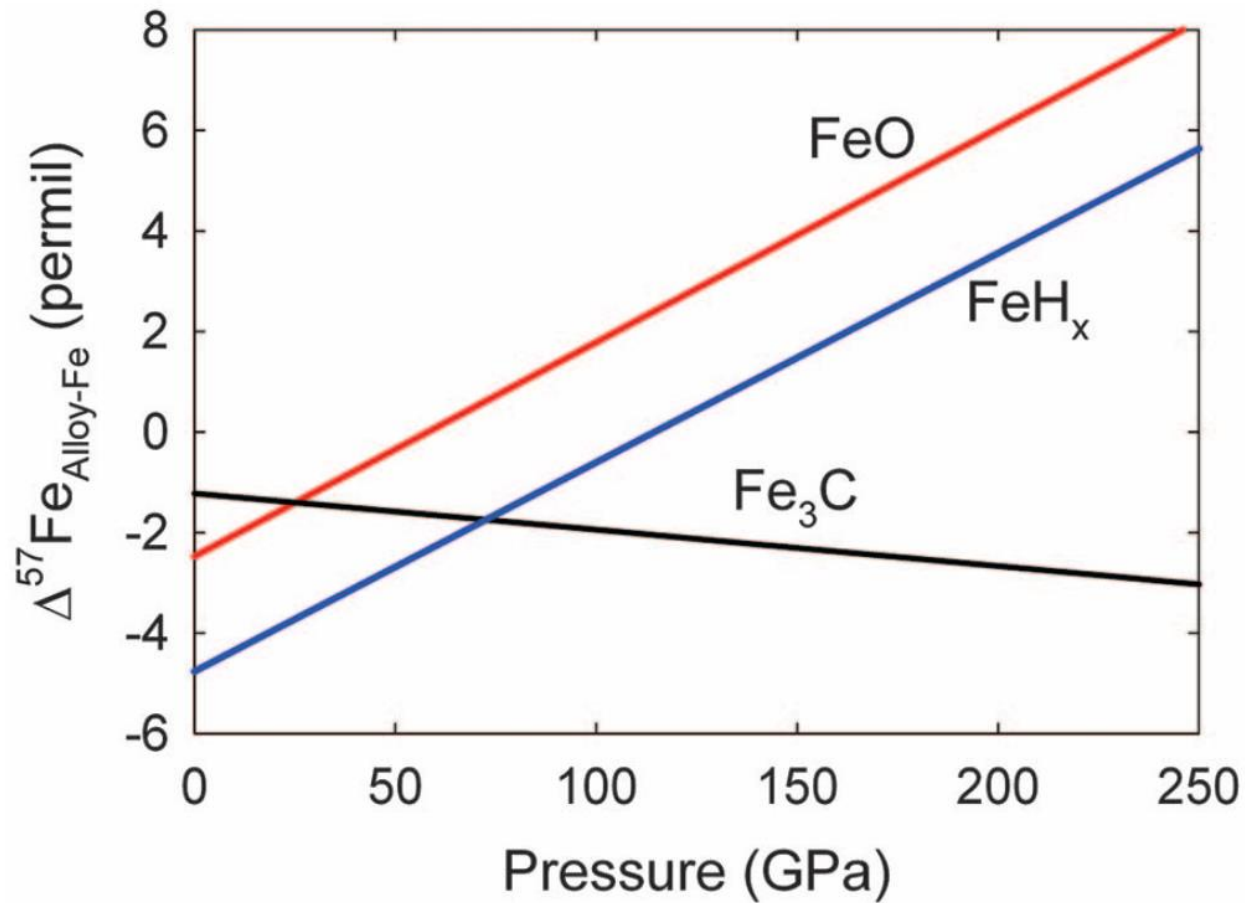
□氧逸度

□不同相的化学组分

$$10^3 \ln \alpha = f(T, P, fO_2, X)$$

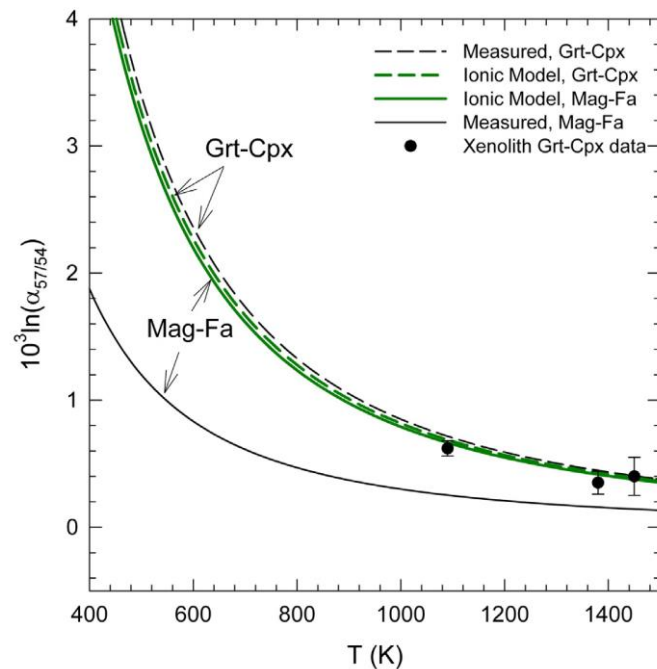
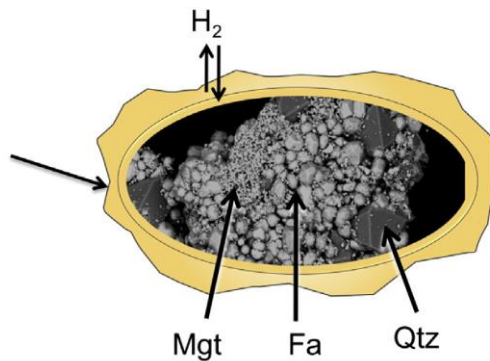
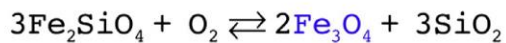
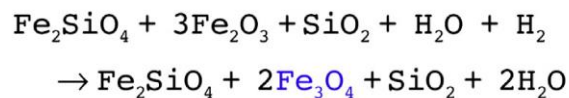
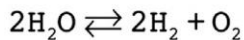
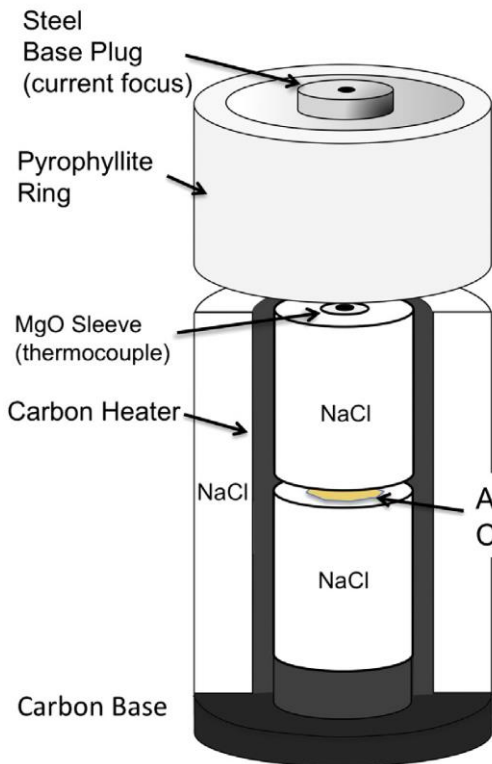
化学键强：化学键短，价态高，配位数低

压力影响铁组分-金属铁之间铁同位素分馏

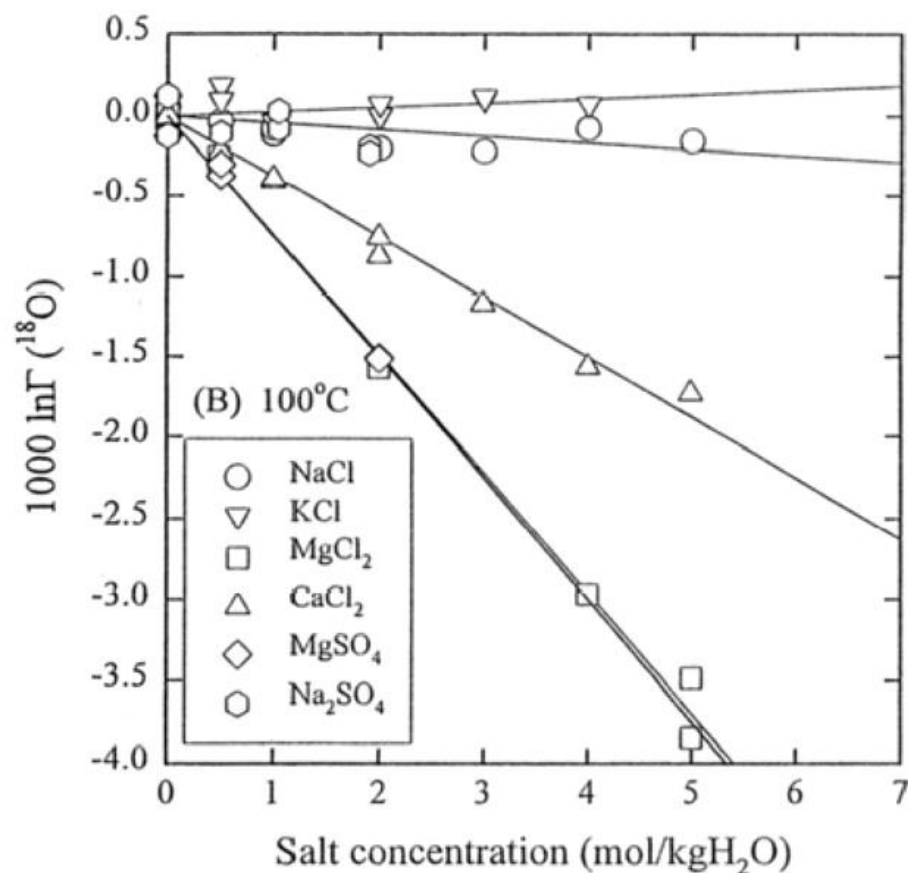
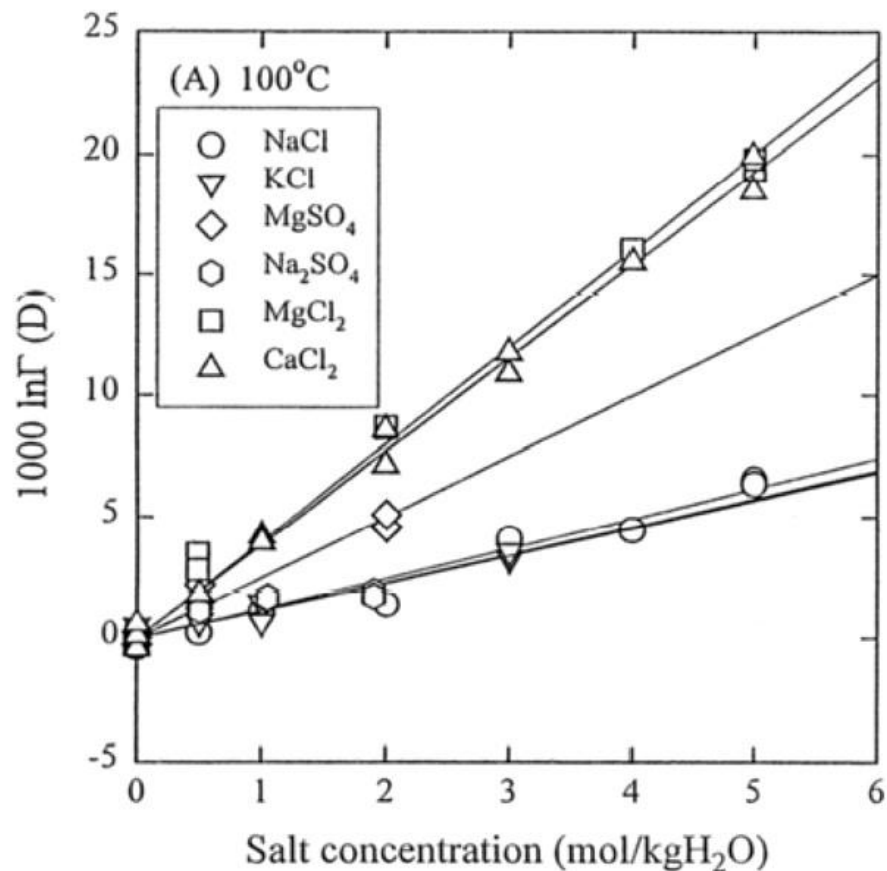


Shahar et al., 2016 Science

氧逸度影响矿物间的Fe同位素分馏



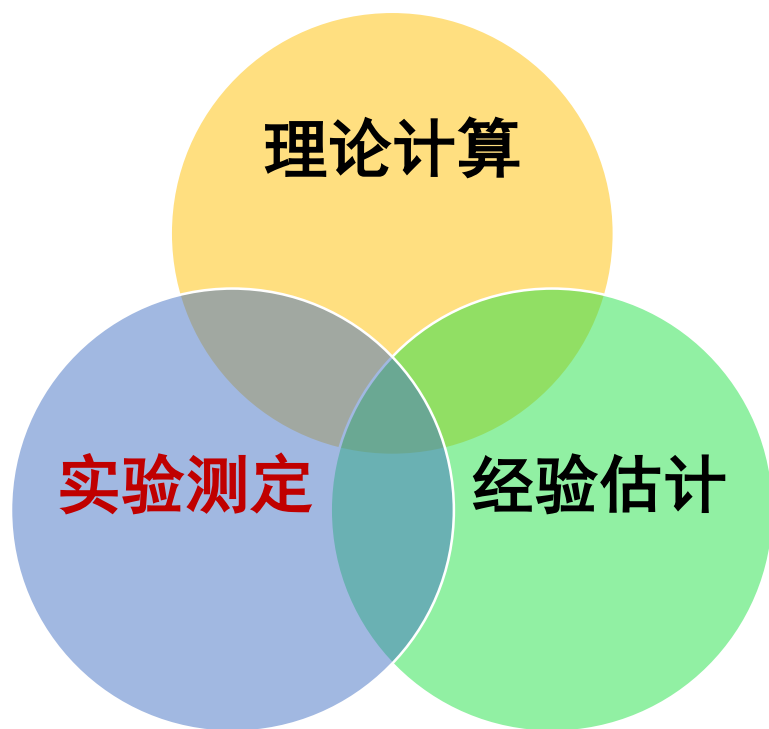
氢、氧同位素分馏的盐效应



$$1000 \ln \Gamma = 1000 \ln \alpha_{v-\text{含盐溶液}} - 1000 \ln \alpha_{v-\text{纯水}}$$

Horita et al., 1994 Conference

同位素平衡分馏系数校准方法



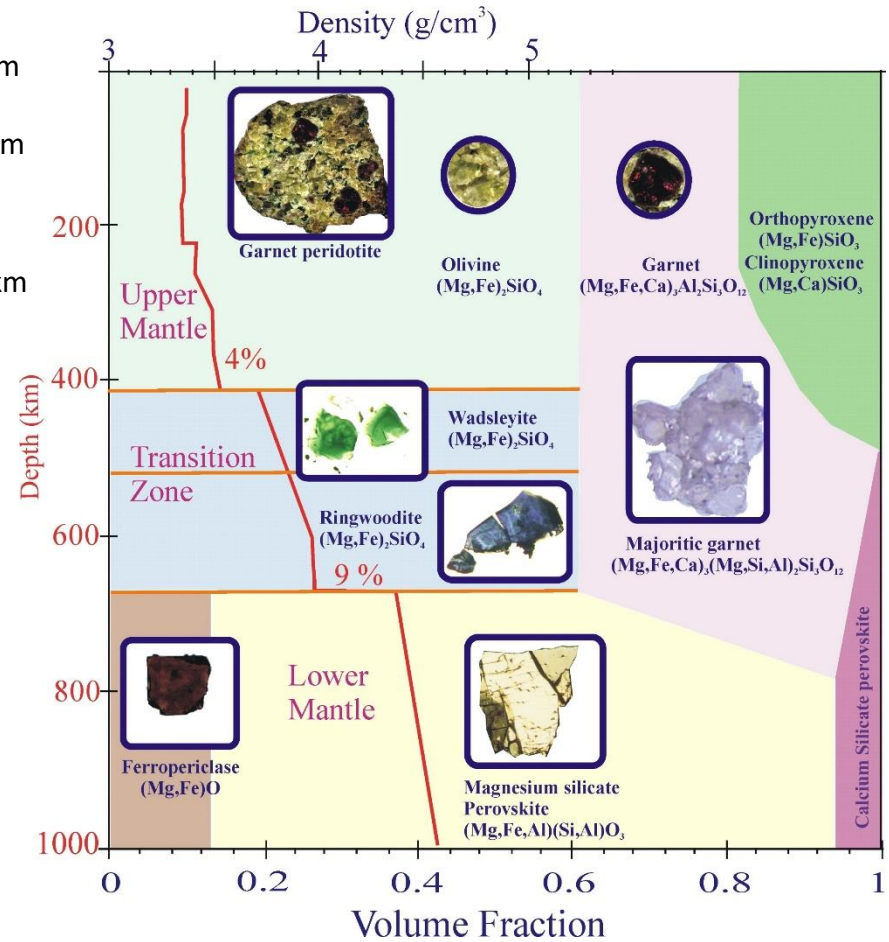
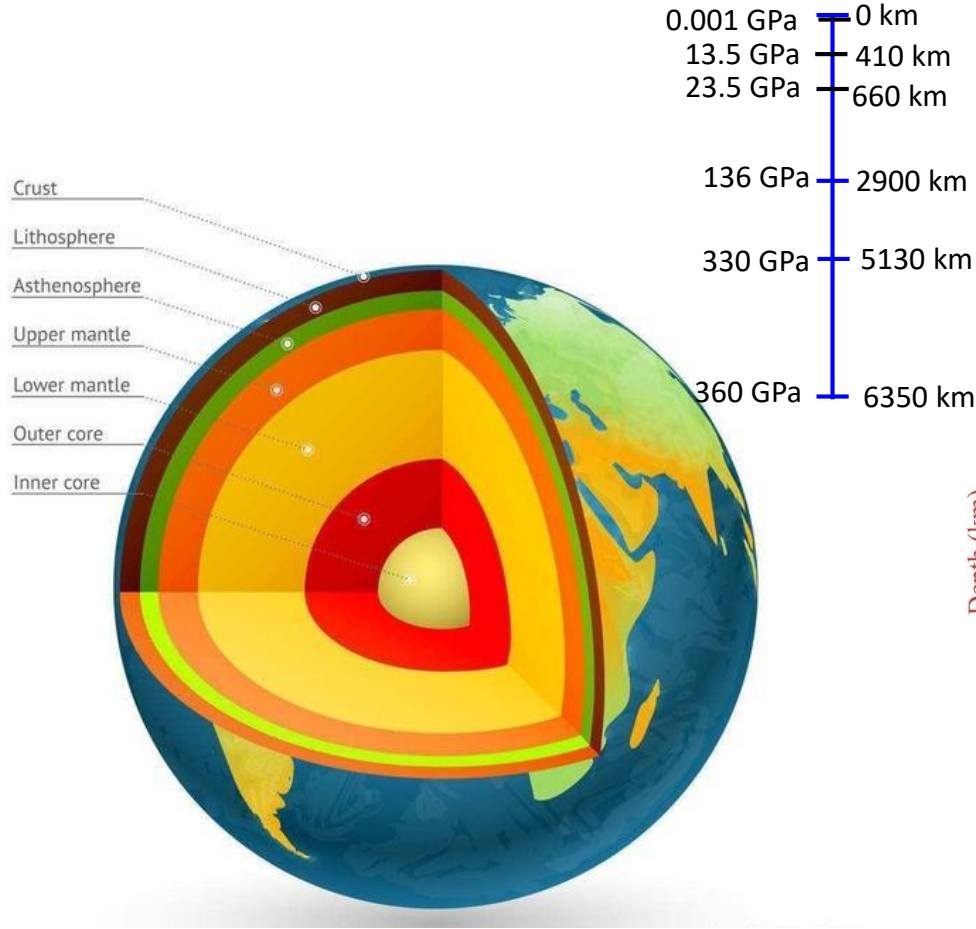
- 统计力学理论，计算不同相的配分函数。
- 实验测定：可靠、直观、耗资费时、实验难度和误差大小。
- 经验估计：直观，接近实际地质条件，平衡？温度估计？
- 各有优缺点，相互补充，印证

$$10^3 \ln \alpha_{A-B} \approx 10^3 (\alpha_{A-B} - 1) \approx \Delta_{A-B} = \delta_A - \delta_B$$

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研究地球内部



1 GPa = 10 kbar = 1000 MPa

地球深部的样品



地幔橄榄岩捕虏体



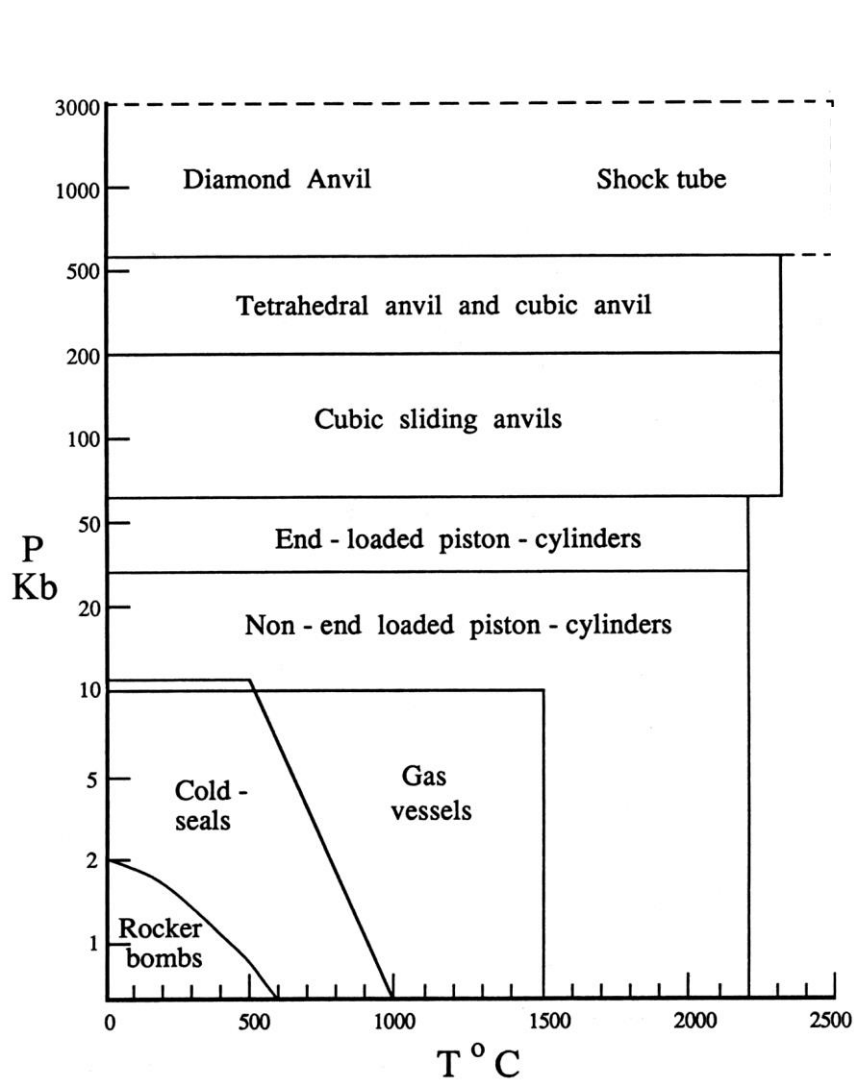
金刚石包裹体

科学超深钻

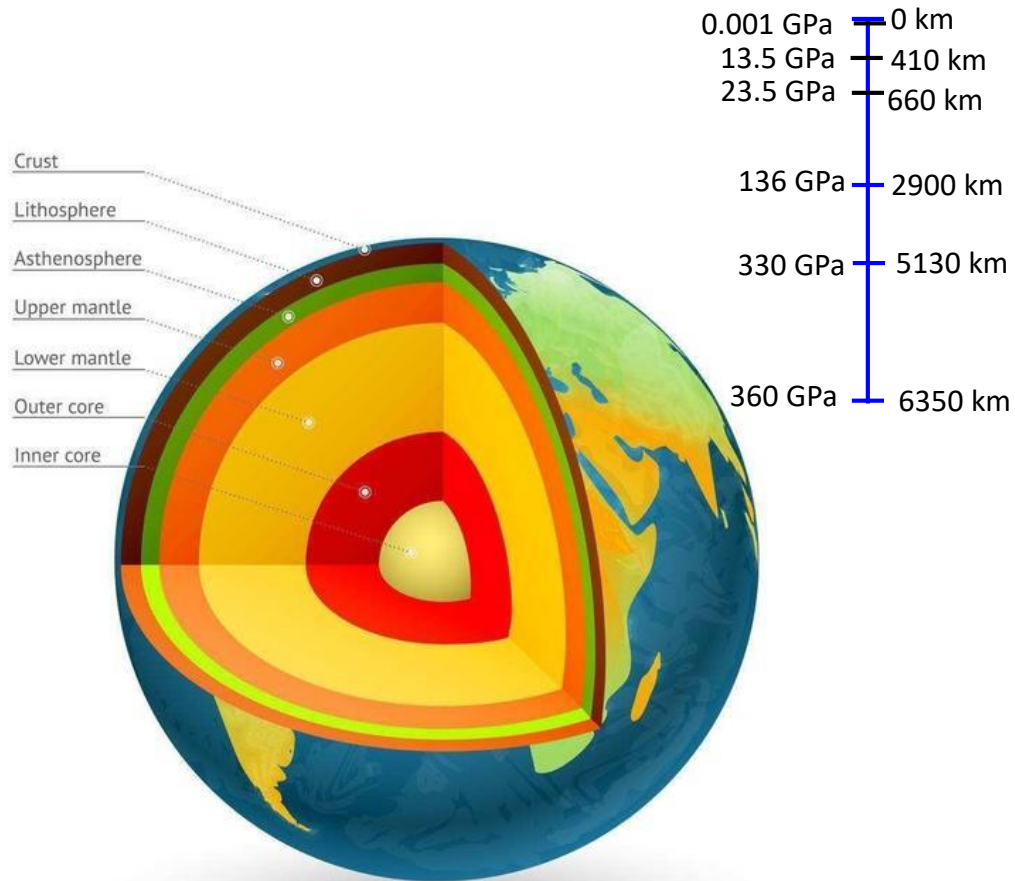


前苏联 科拉超深钻孔

高温高压实验模拟地球内部



1 GPa = 10 kbar = 1000 MPa



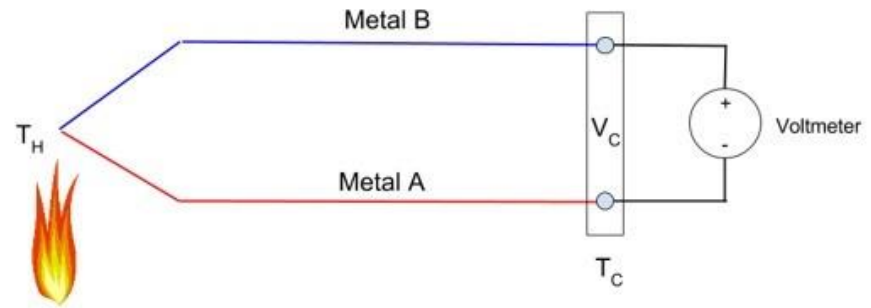
- 实验岩石学
- 实验地球化学
- 矿物物理学
-

高温炉



Gas mixing furnace

1 bar / 1700 °C

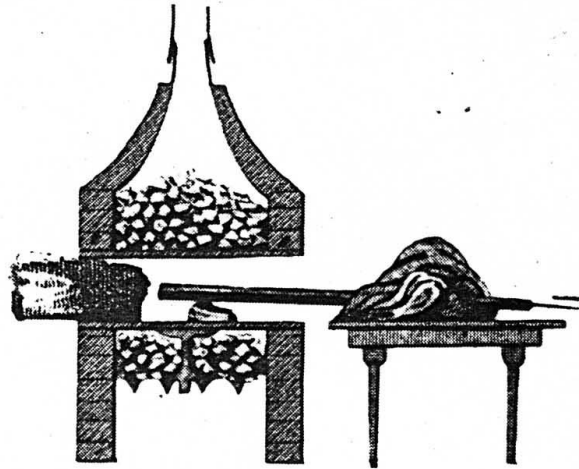
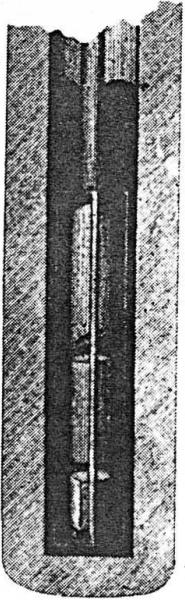
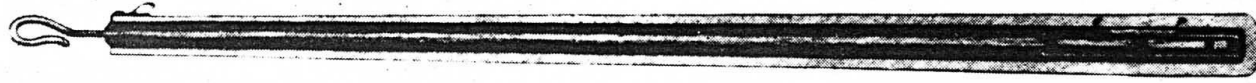


热电偶 (thermocouples) 测温

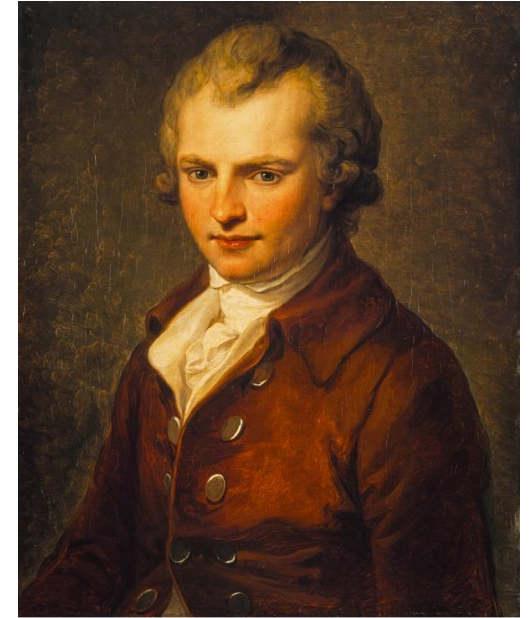
- Type K: Chromel (90% Ni and 10% Cr)
- Alumel (95% Ni, 2% Mn, 2% Al and 1% Si)
- Type S: Pt-Pt₉₀Rh₁₀
- Type D: W₉₇Re₃-W₇₅Re₂₅
- Type C, E, R.....

Thermocouples	Chromel/Alumel (type k)	1150 (reducing or oxidizing atm.)
	Platinum/Platinum 10 Rhodium (type S)	1450 (oxidizing atmosphere)
	Pt/Pt 10 Rh (type S)	1150 (reducing, carbonaceous atmosphere)
	Tungsten 5/Rhenium-Tungsten 25 Rh (reducing atmosphere)	2200

最早的高温高压实验



Sir James Hall
(1761 - 1832)

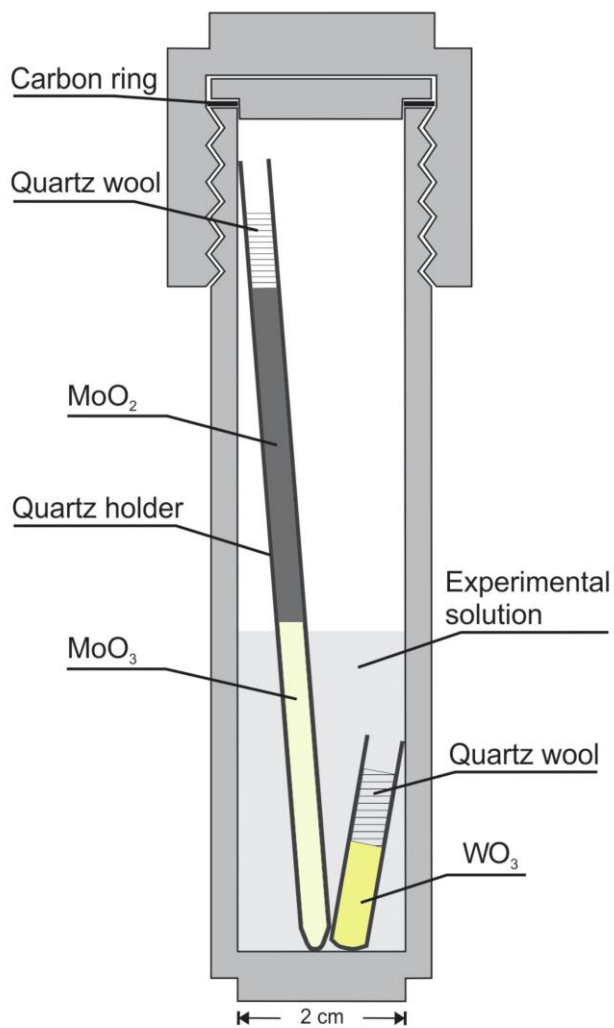


NATIONAL GALLERIES SCOTLAND
Sir James Hall of Dunglass, 1761 - 1832. Geologist, 1785, Angelica Kauffmann
Photography by Antonia Reeve
Creative Commons - CC by NC

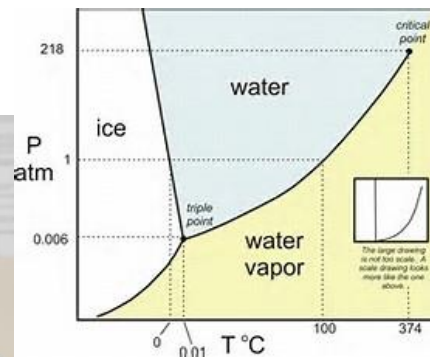
高温高压实验的发明者：

地质学家！

高压釜



~200 bar / 350 °C



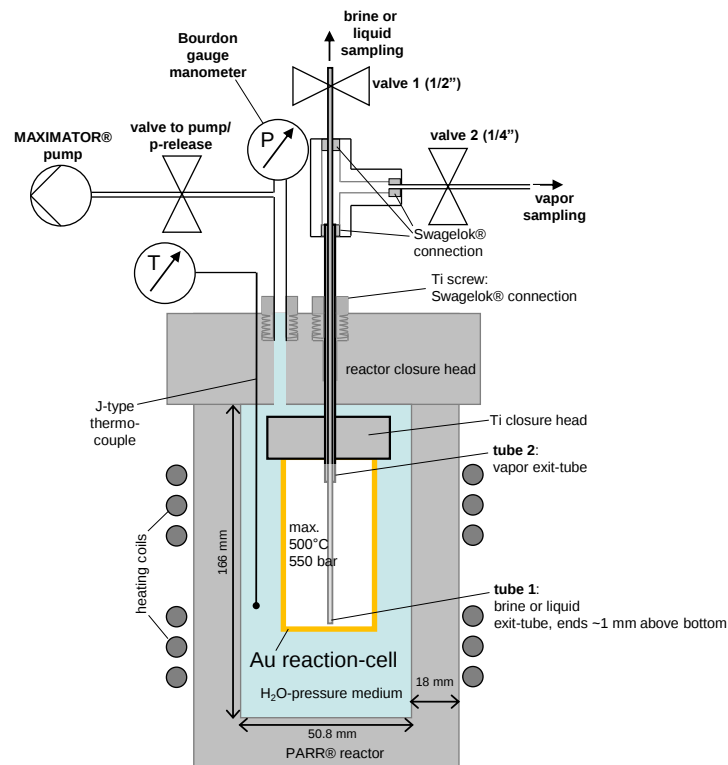
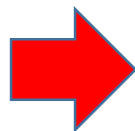
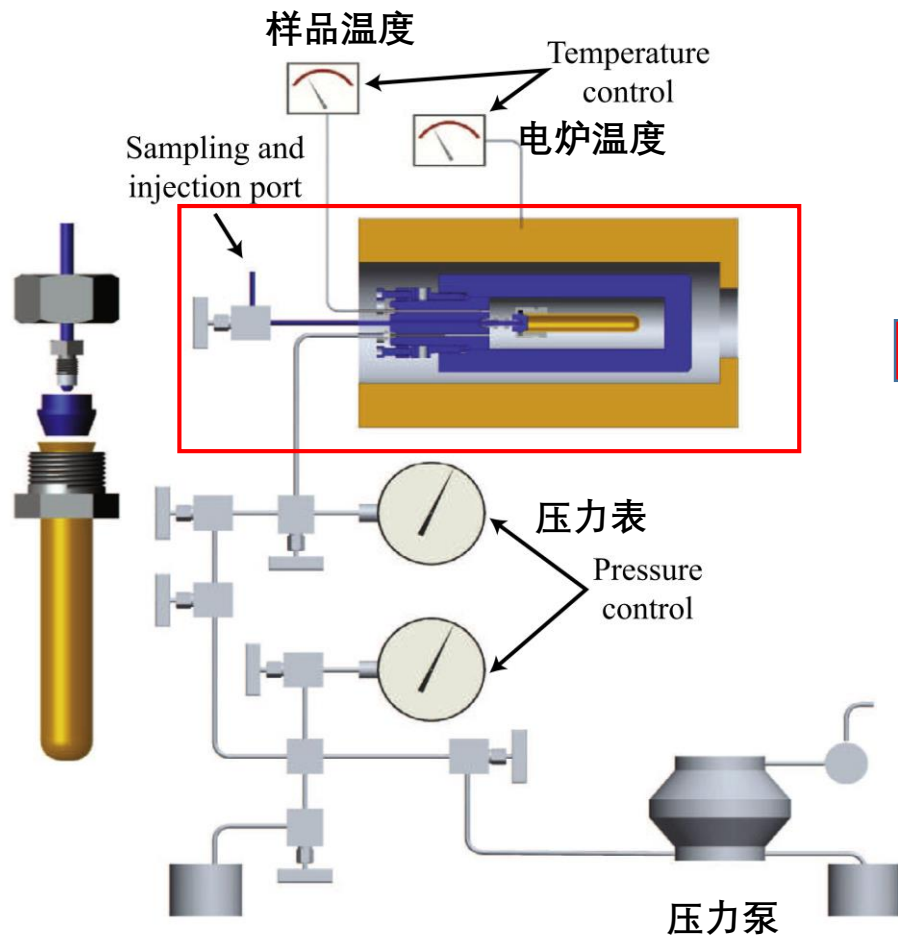
- 优点: 造价低廉, 使用方便, 样品体积大, 可以同时多组实验
- 缺点: 温压局限, 只能饱和蒸汽压控制, 只适合流体体系, 不能单独控制温度压力

高压釜

金内衬

可以单独控制温度-压力

可以原位注入，提取样品



550 bar / 550 °C

Syverson et al., 2018 GCA

Photo from Beermann, Kiel

高压釜的材料

Ni alloy- Rene 41; Nimonic-90



TZM-Titanium, Zirconium, Molybdenum

MHC-Molybdenum Hafnium Carbide

压力介质

水

气体: Ar; Ar-H₂



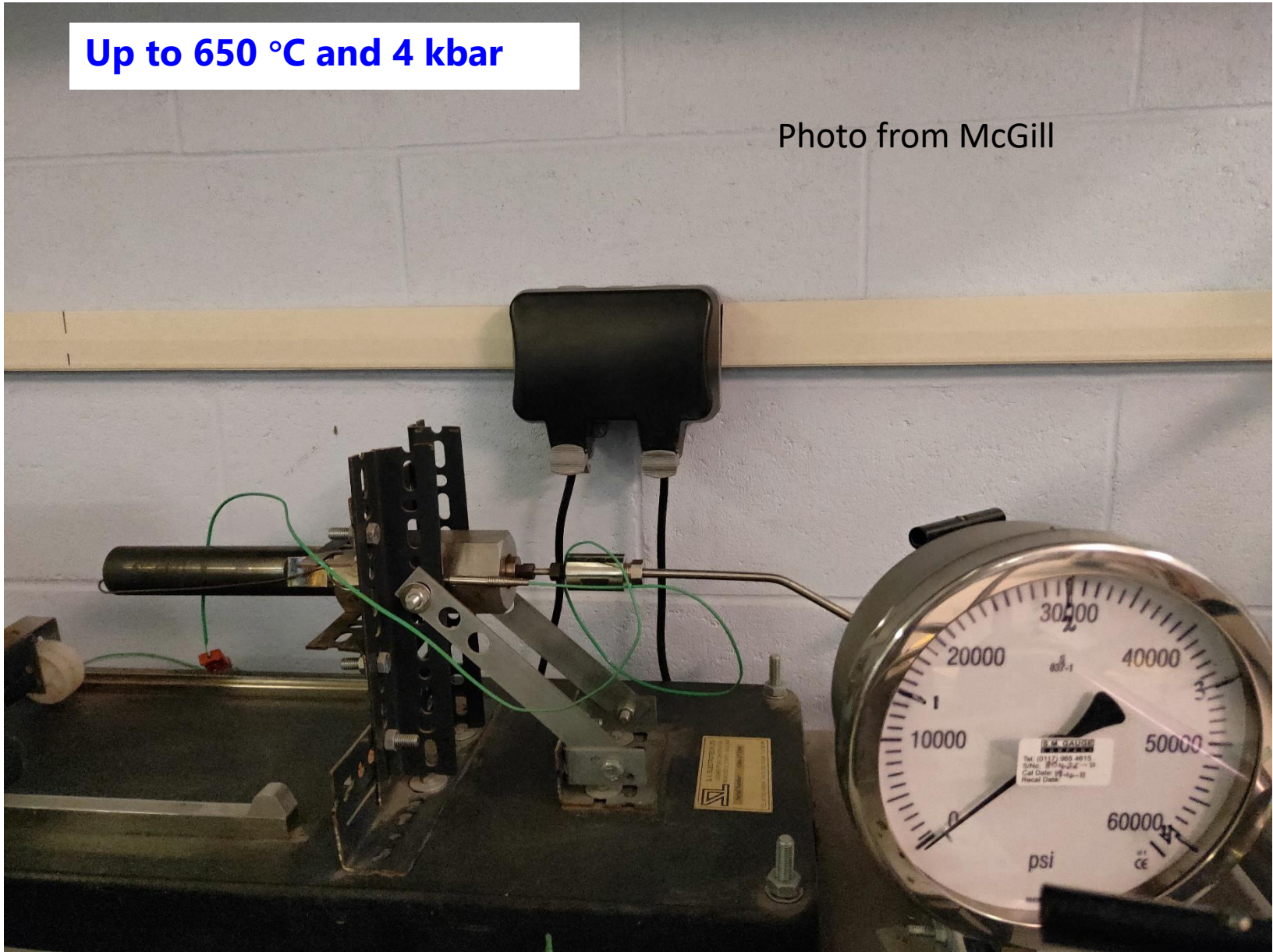
压力控制系统-水（气）加压



冷封式高压釜-横式

Up to 650 °C and 4 kbar

Photo from McGill



快速淬火式冷封式高压釜

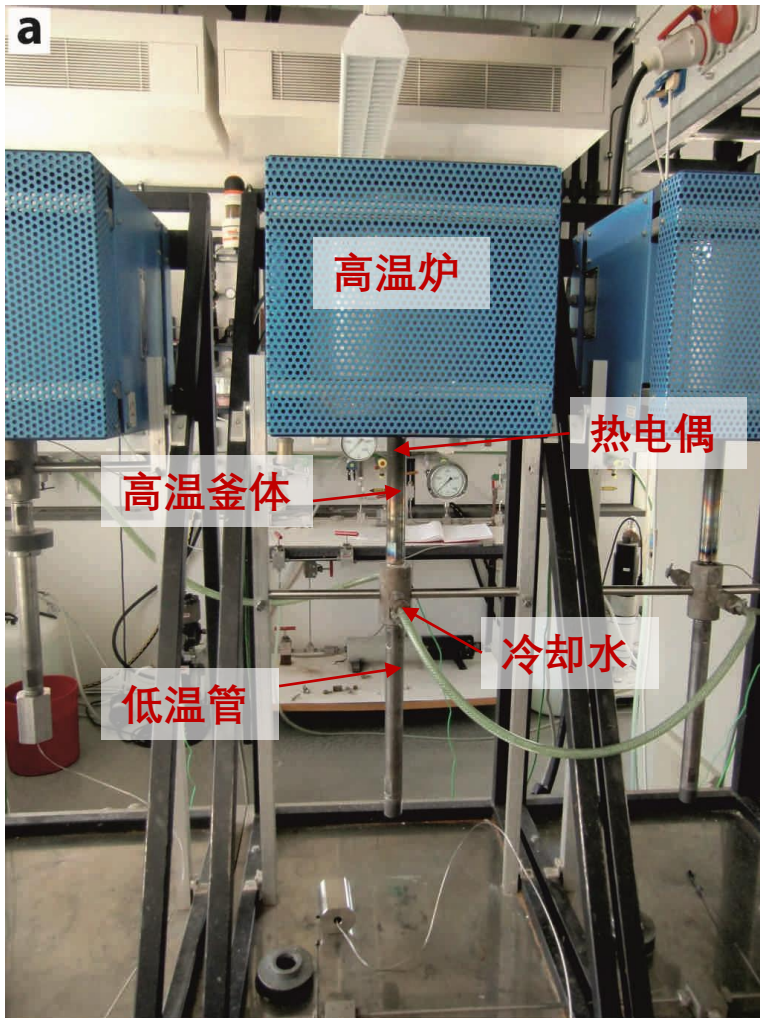
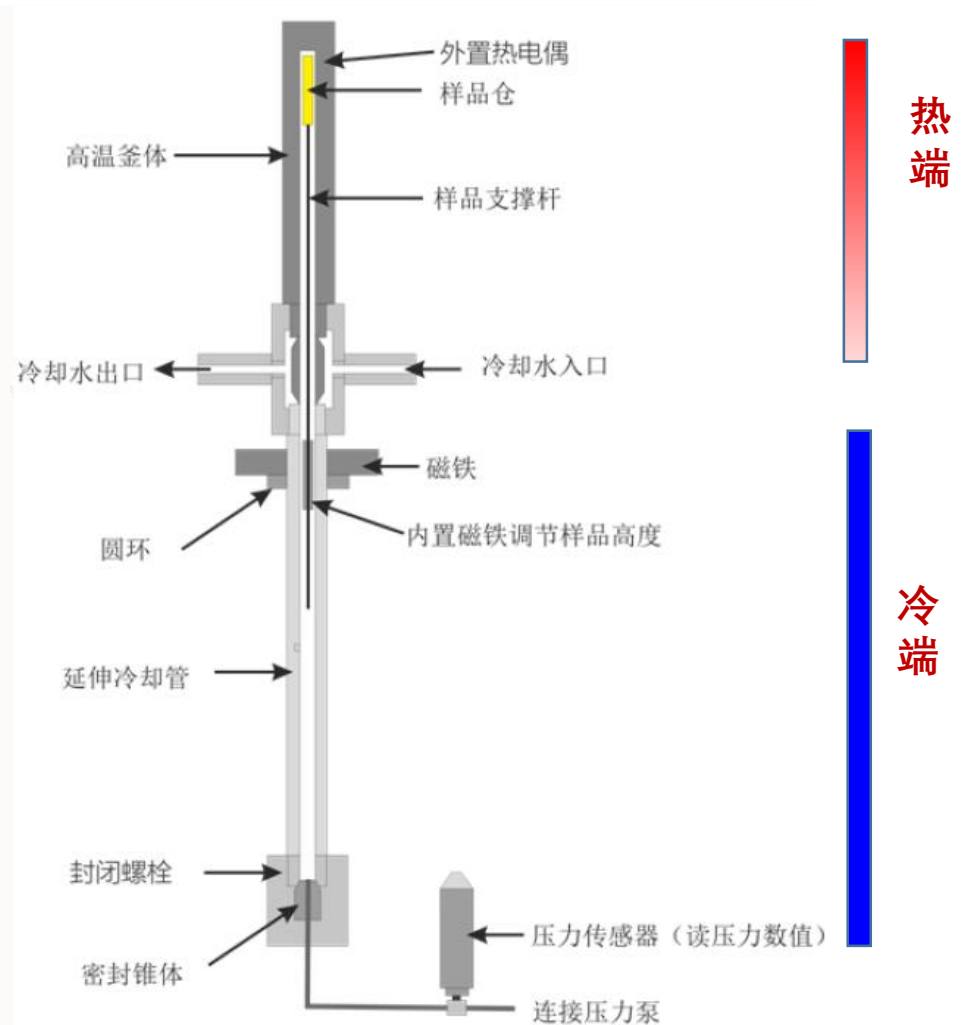


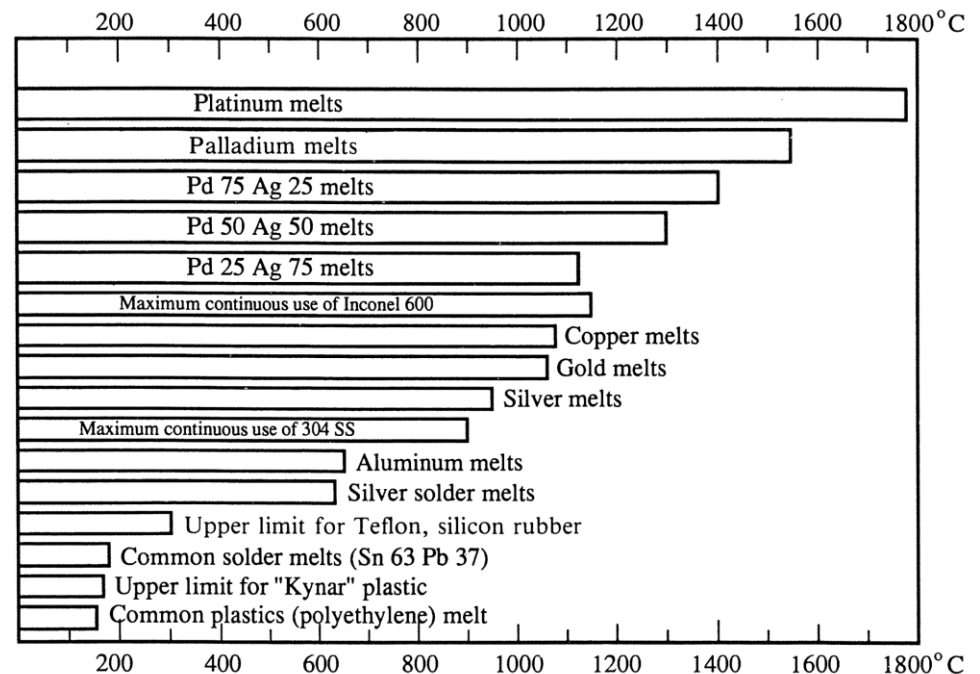
Photo from BGI

Up to 900 °C and 2 kbar

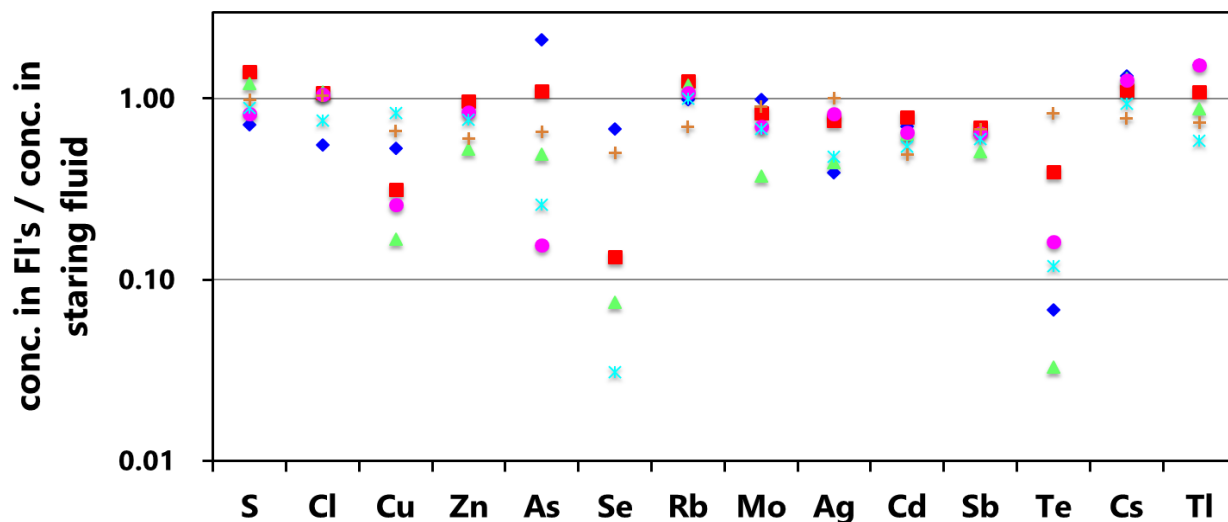


样品管材料-实验的“容器”

	Au	Pt	Ag	Pt ₉₅ Rh ₅	Au ₈₀ Pd ₂₀
Melting point (°C)	1064.18	1768.3	961.8	>1700	~1400
Alloy with Fe	No	Yes	No	Yes	a bit
Alloy with Cu	Yes	yes	Yes	yes	Yes
React with S	No	Yes	Yes	Yes	Yes

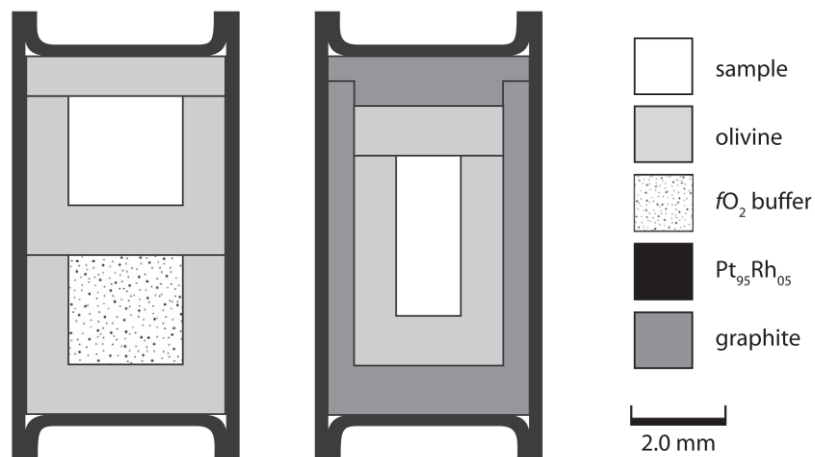


避免金属络合的样品管材料

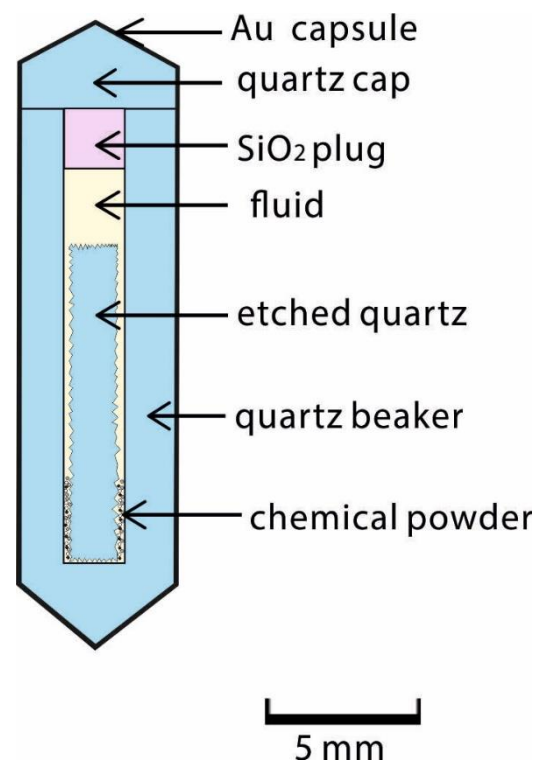


金样品管中

850 °C, 2 kbar, 7 days



Li & Audetat, 2013 GCA



after Lerchbaumer & Audetat, 2012 EJM

石英, 石墨, 橄榄石, 氧化镁样品管.....

实验原料



实验药品作为起始物质，简化研究体系

怎么添加微量成分

干体系vs.湿体系

固体药品vs.溶液加入

不挥发元素vs. 挥发元素

溶液中不同物质样品互相沉淀怎么办？

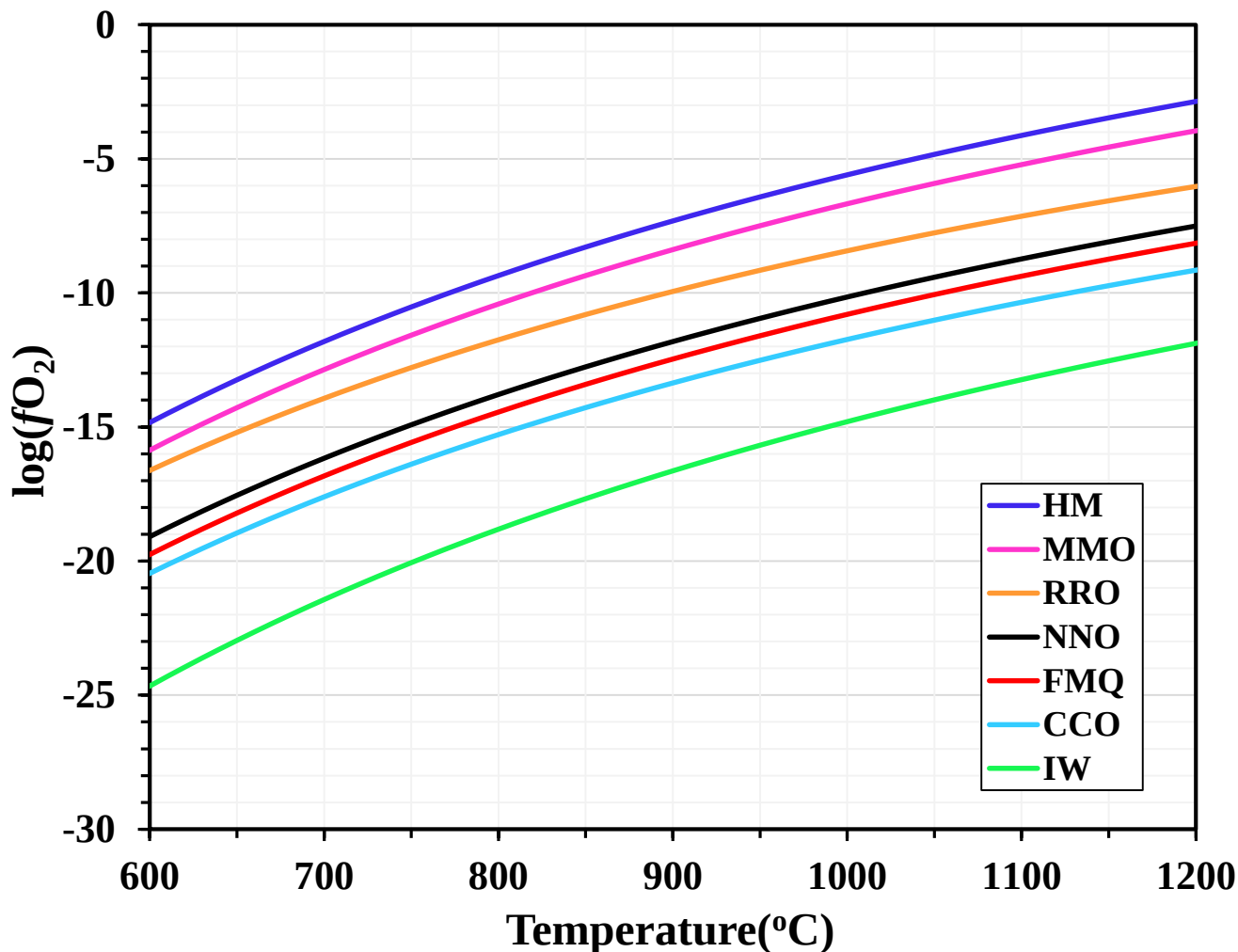
Solution No.	Components	Concentrations
A	H_2SO_4 , HCl , LiCl , CuCl_2 , ZnCl_2 , CdCl_2 , SbCl_3	$\text{S} \sim 10\text{wt}\%$, $\text{Cl} \sim 6.6\text{wt}\%$, $\text{Li}, \text{Cu}, \text{Zn}, \text{Cd}, \text{Sb} \sim 3000\text{ppm}$
B	H_2SO_4 , HCl , $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$, Na_2TeO_4 , NaBr	$\text{S} \sim 10\text{wt}\%$, $\text{Cl} \sim 6.6\text{wt}\%$, $\text{Br} \sim 0.5\text{wt}\%$, $\text{Se}, \text{Te} \sim 3000\text{ppm}$
C	H_3BO_3 , As_2O_3 , TlCl	$\text{B}, \text{As}, \text{Tl} \sim 3000\text{ppm}$

不溶解的元素可以用ICP溶液后蒸干去除水和硝酸



常用的氧逸度缓冲剂

地质上常表示为 $\Delta\text{FMQ} \pm X$; $\Delta\text{IW} \pm X$



HM: hematite-magnetite

MMO: $\text{MnO-Mn}_3\text{O}_4$

RRO: Re-ReO_2

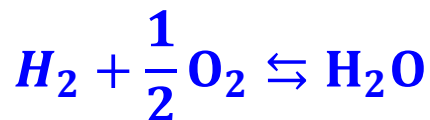
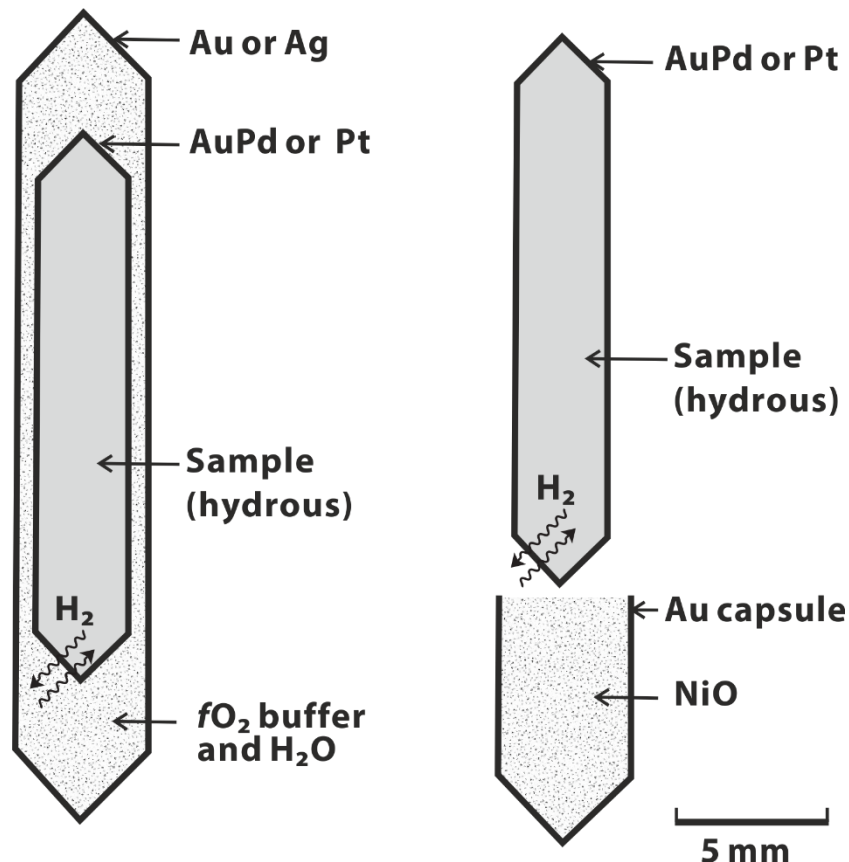
NNO: Ni-NiO

FMQ: fayalite-magnetite-quartz

CCO: Co-CoO

IW: iron-wustite

双样品管法



NNO: Ni-NiO

RRO: Re-ReO₂

MMO: MnO-Mn₃O₄

HM: hematite-magnetite

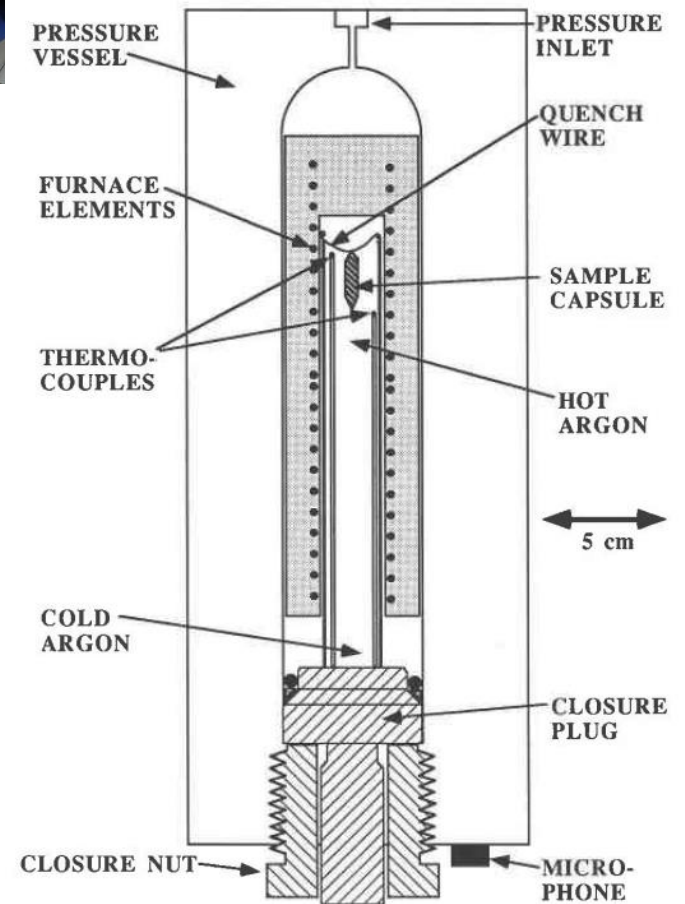
FMQ: fayalite-magnetite-quartz

CCO: Co-CoO

IW: iron-wustite

H_2 的通透性: $Au_{80}Pd_{20} > Pt \gg Ag > Au$

内加热高压釜



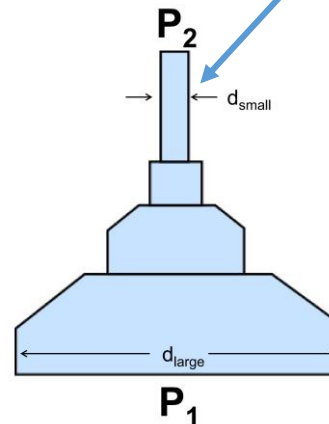
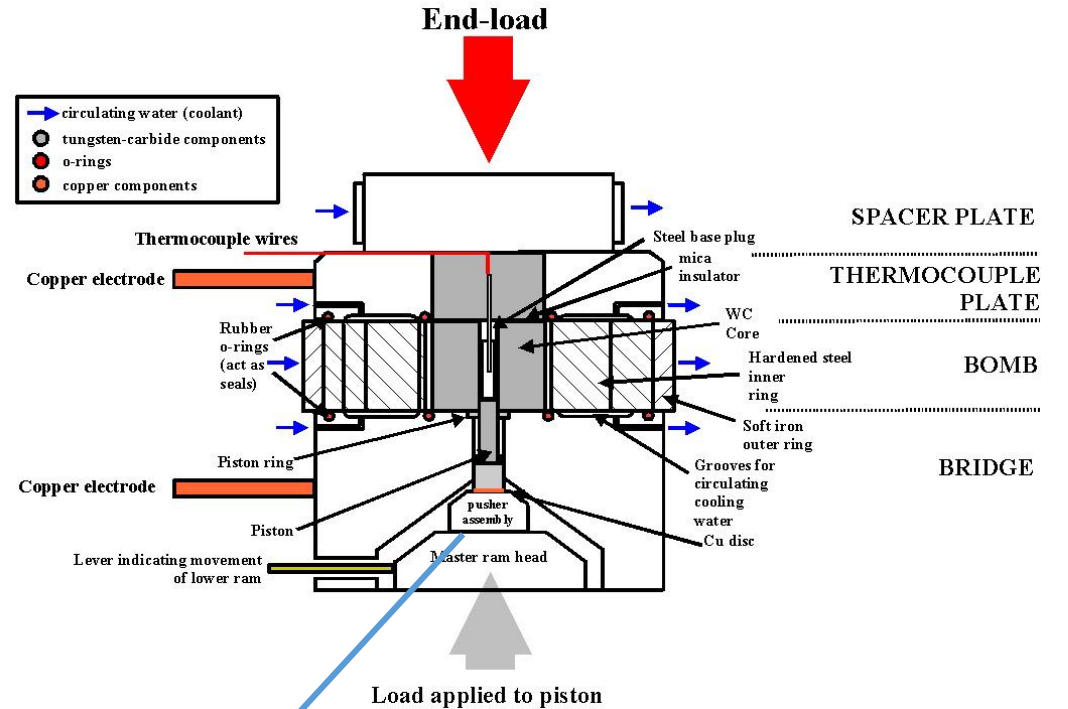
Internally heated pressure vessel (IHPV)
10 kbar / 1200 °C

Holloway et al., 1992 AM

活塞圆筒压机



Piston cylinder apparatus
6 GPa (60 kbar)
1700 °C



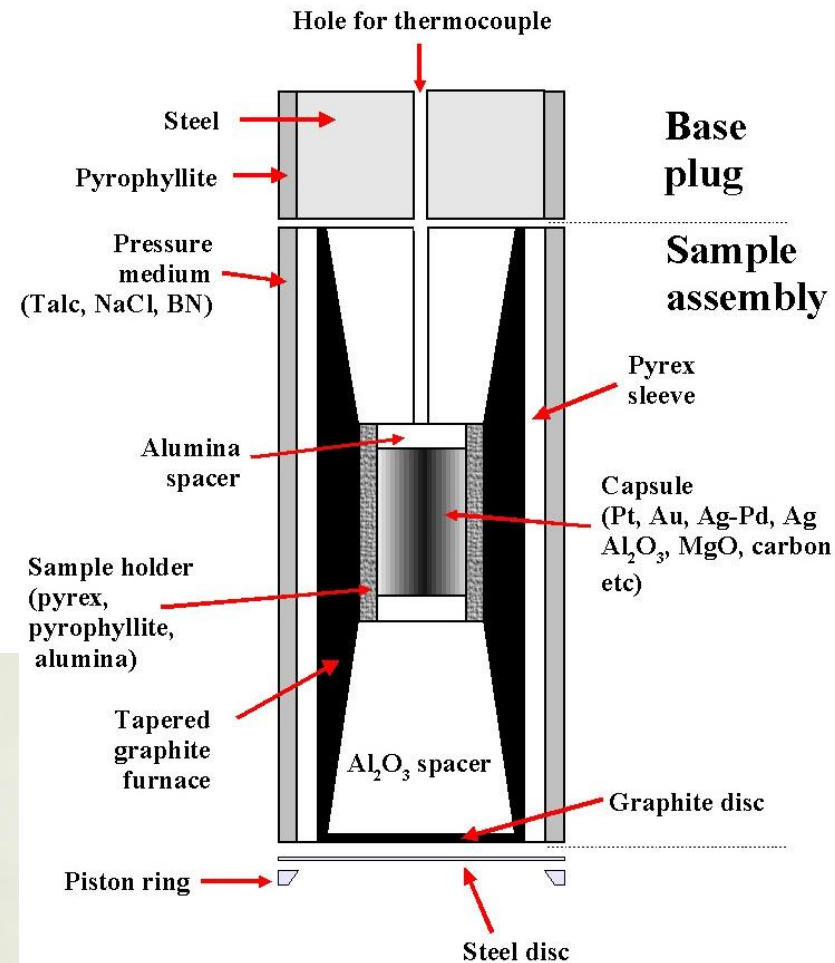
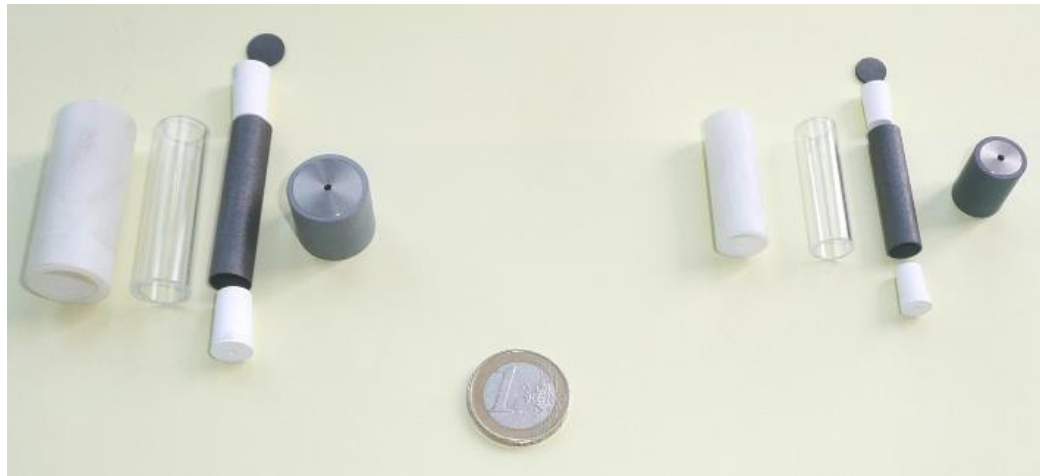
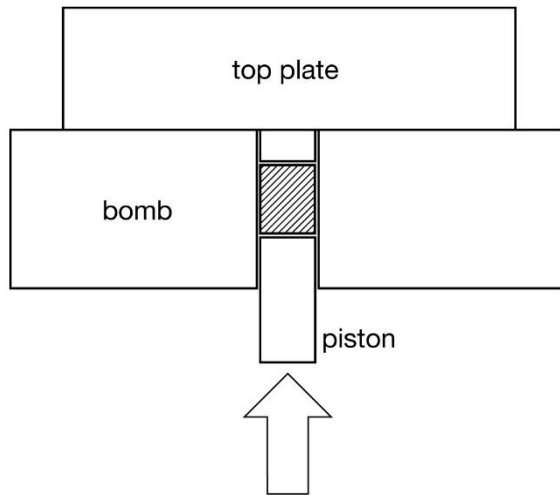
压强 = 压力 / 面积 $P = F/S$

$$P_1 d_{\text{large}}^2 = P_2 d_{\text{small}}^2$$

$P_1 = 488 \text{ bar} \rightarrow P_2 = 40 \text{ kbar}$

Diagrams from BGI

活塞圆筒压机样品组装



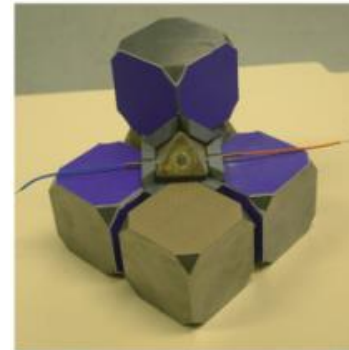
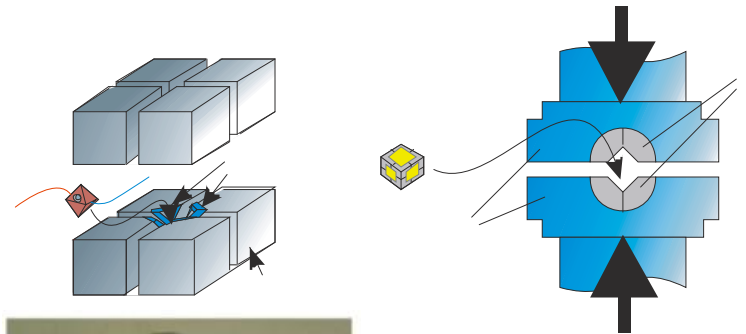
Diagrams from BGI

多面砧压机（大压机）

100 tonf = 980000 N = 0.98 MN



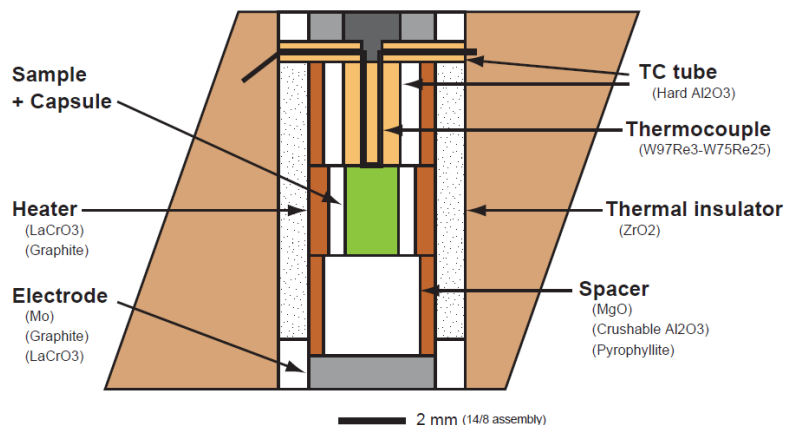
Photo from BGI



Multi-anvil press (large-volume press)
25 GPa (250 kbar)
3000 °C

压力校正

样品组合



内部模块

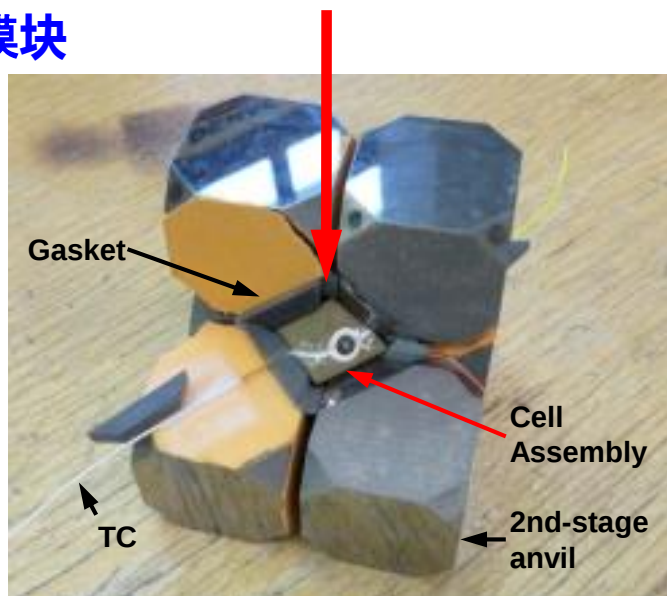
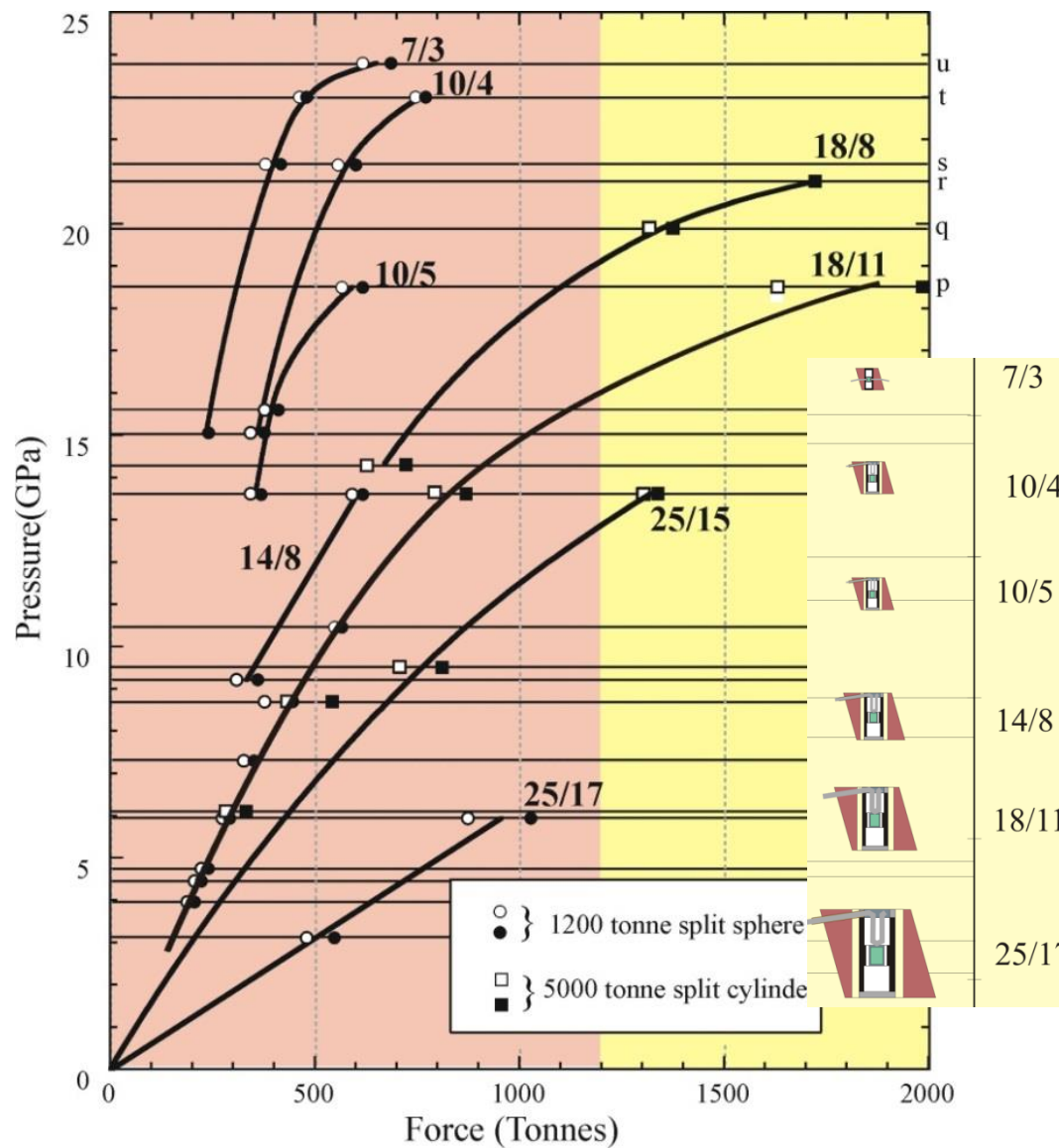


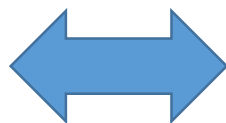
Photo from Dr. Takaaki Kawazoe



Keppler & Frost (2005), EMU Notes in Mineralogy

产生高压策略

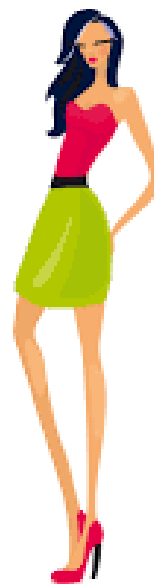
$$P = F / S$$



$$P = F / s$$



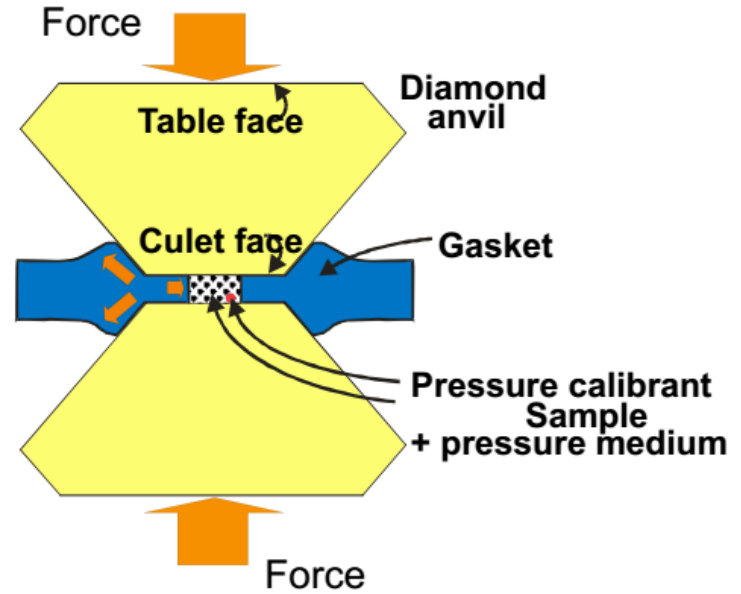
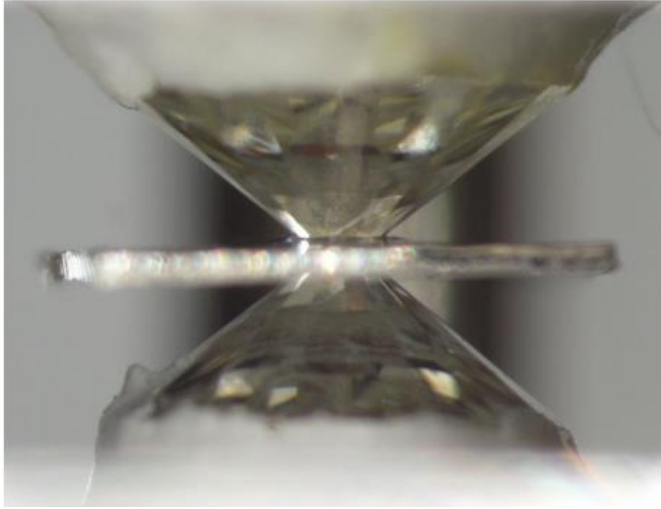
地面压强 P



地面压强 P



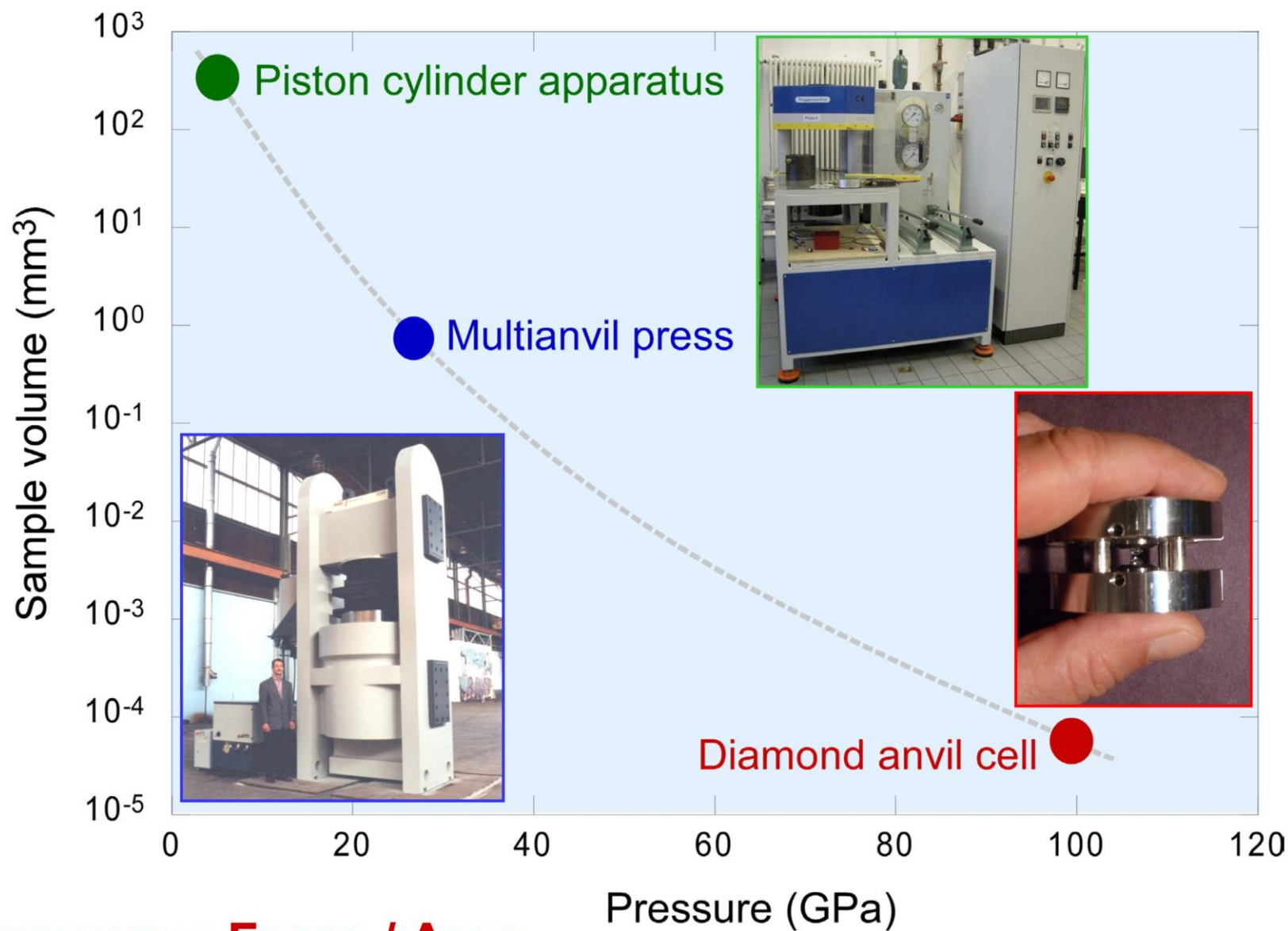
金刚石压砧（小压机）



Diamond anvil cell
(DAC)

>100 GPa (> 1 Mbar)
> 5000 °C

压强和样品体积关系



Pressure = Force / Area

from BGI short course

做好实验研究的一些总结

- *Well-defined question*
- *Keep the system simple*
- *Pay attention to minor things*
- *Do not discard unexpected results*

-Hans Keppler

休息一会儿
(Questions?)

摘要

1. 稳定同位素分馏理论简介
2. 高温高压实验方法介绍
3. 实验测定同位素分馏原理
4. 实验研究实例

实验测定同位素平衡分馏系数

➤ 熔体-熔体 （金属，硅酸盐，硫化物…）

-核幔分异，岩浆演化熔体不混融

➤ 熔体-矿物

-岩浆结晶分异

➤ 矿物-矿物

-岩浆、变质过程，地幔矿物平衡

➤ 熔体-流体

-流体出溶， 岩浆热液

➤ 流体-矿物

-流体中矿物沉淀，结晶

➤ 流体-流体 （流体不混溶）

-流体沸腾，液态不混溶

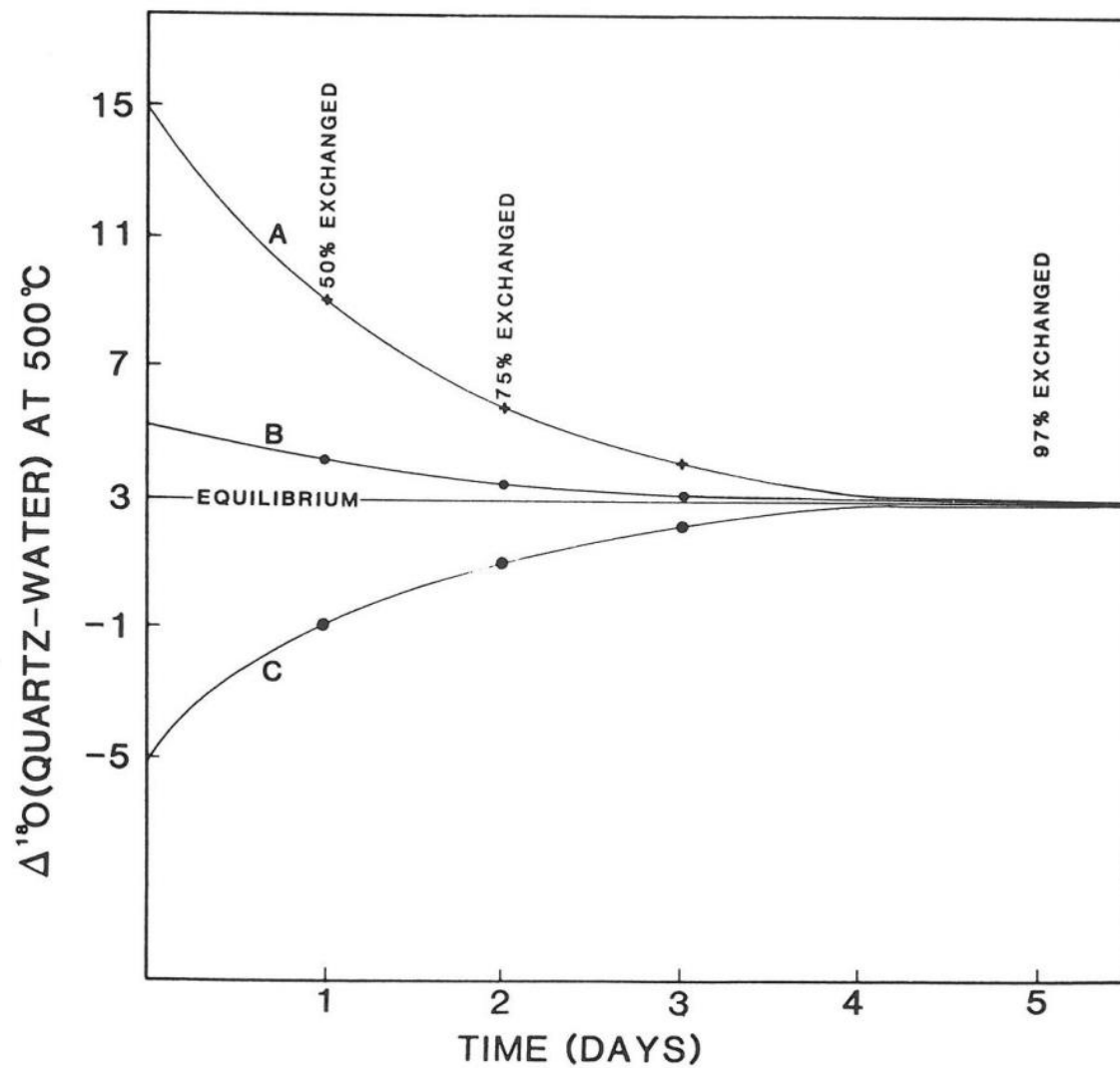


两相分离！

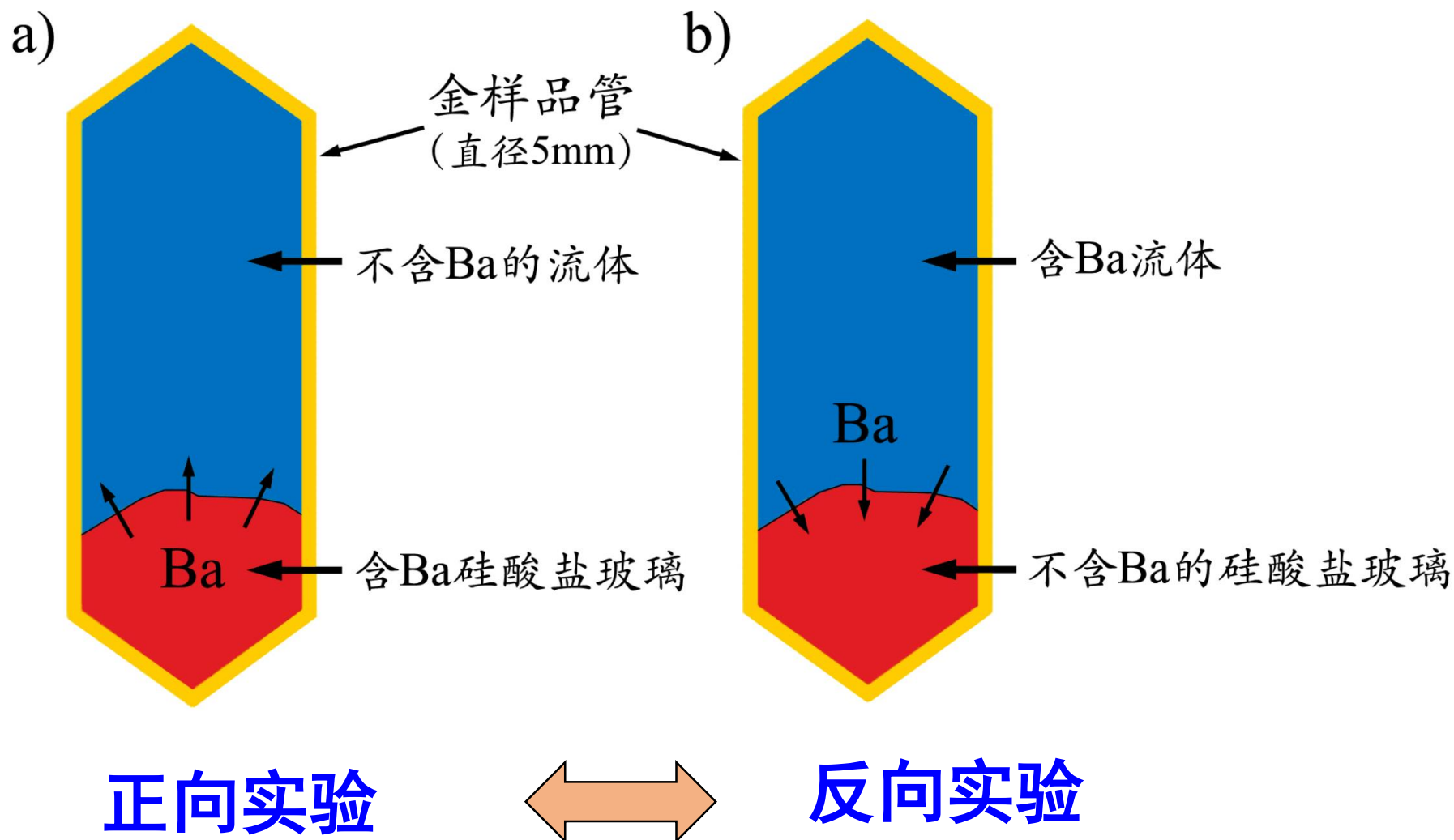


实验平衡！

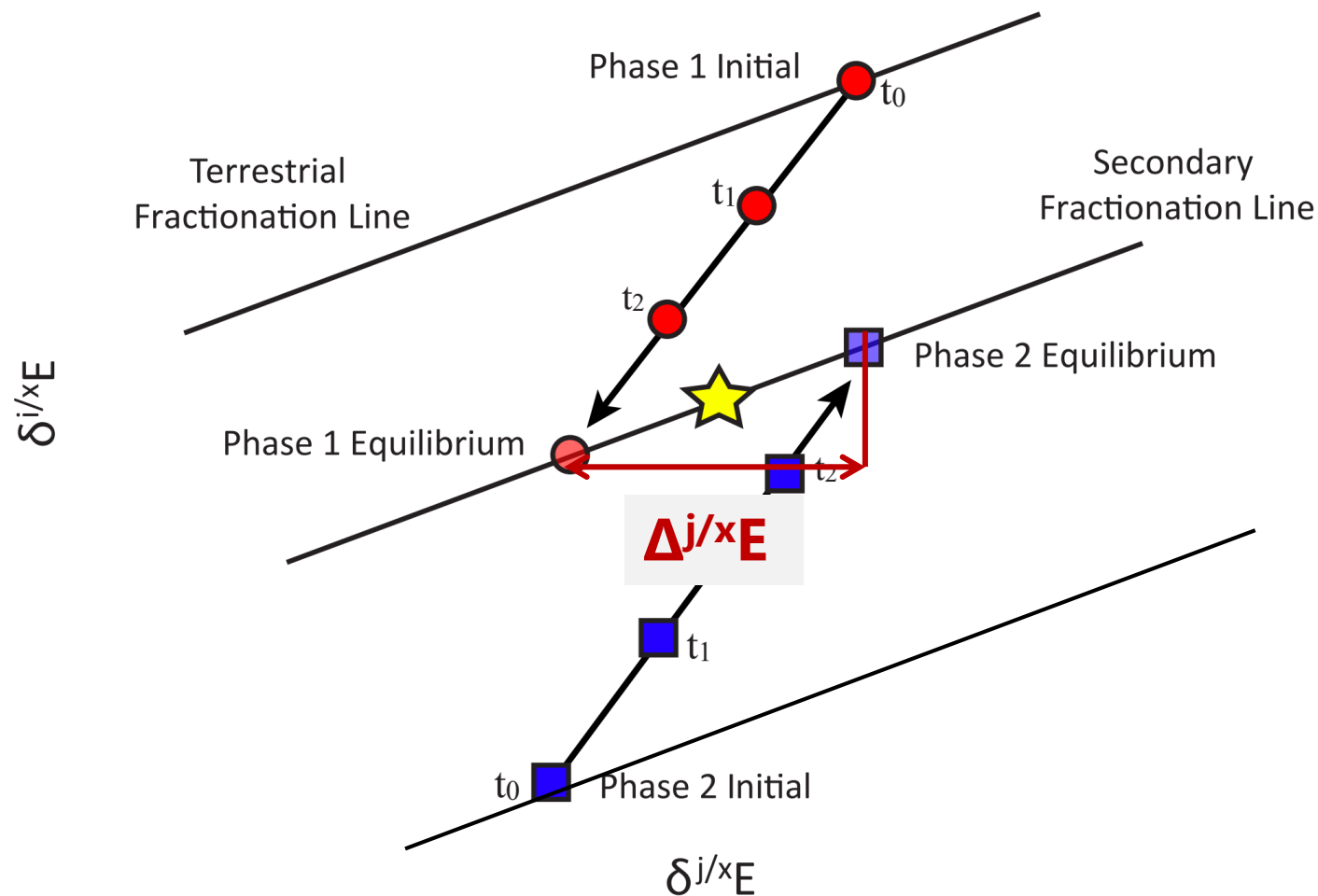
判断平衡 (1) -时间序列



判断平衡（2）-正反向实验



判断平衡 (3) - 三同位素法



实验研究同位素动力学分馏

➤ 扩散过程（熔体，矿物，流体...）

-热梯度，浓度梯度...

➤ 快速结晶

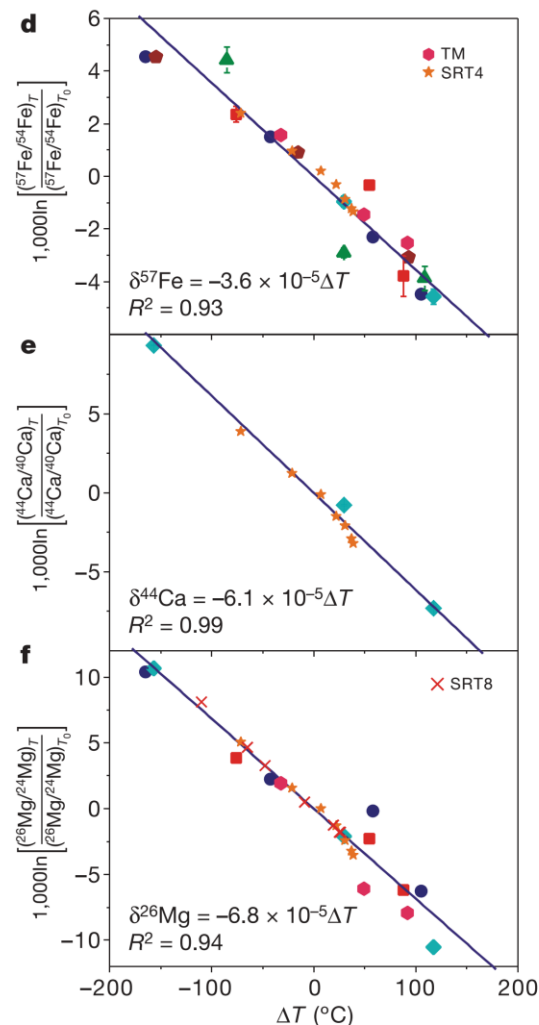
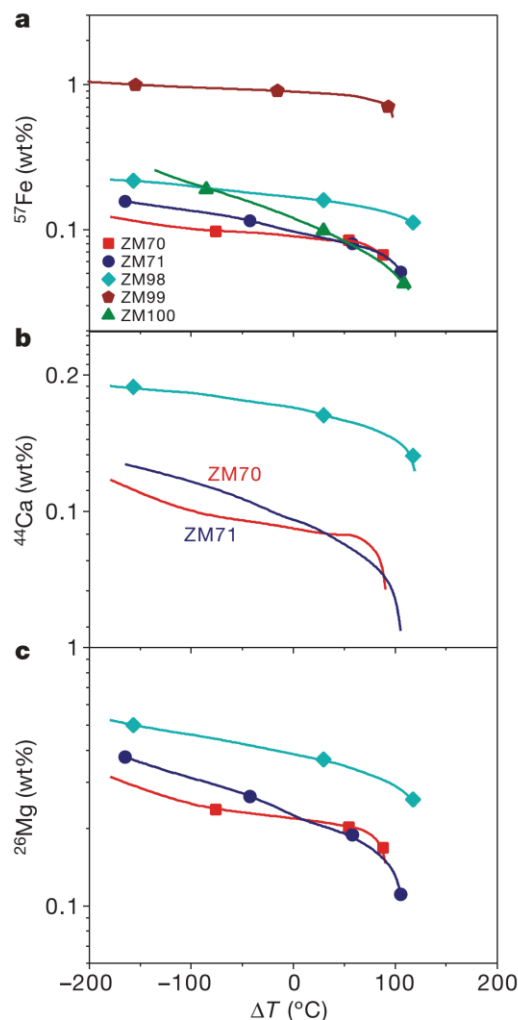
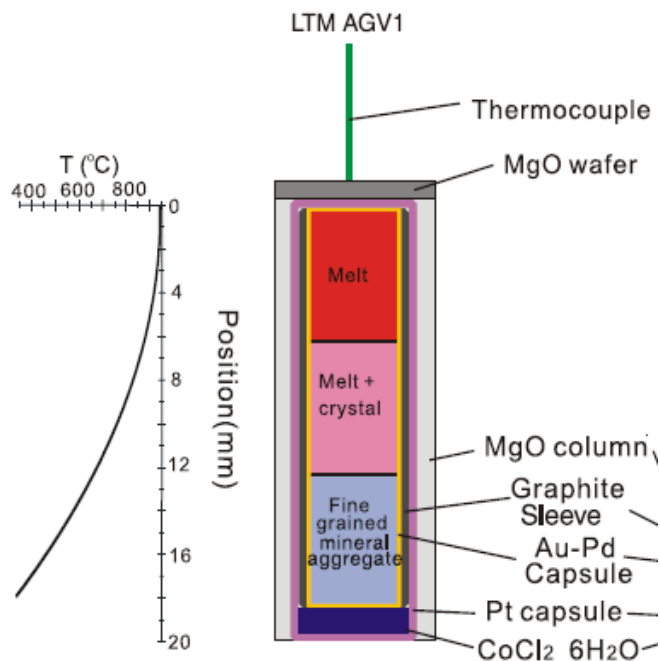
-岩浆，流体快速冷却

➤ 挥发过程

-岩浆去气，地球早期元素挥发

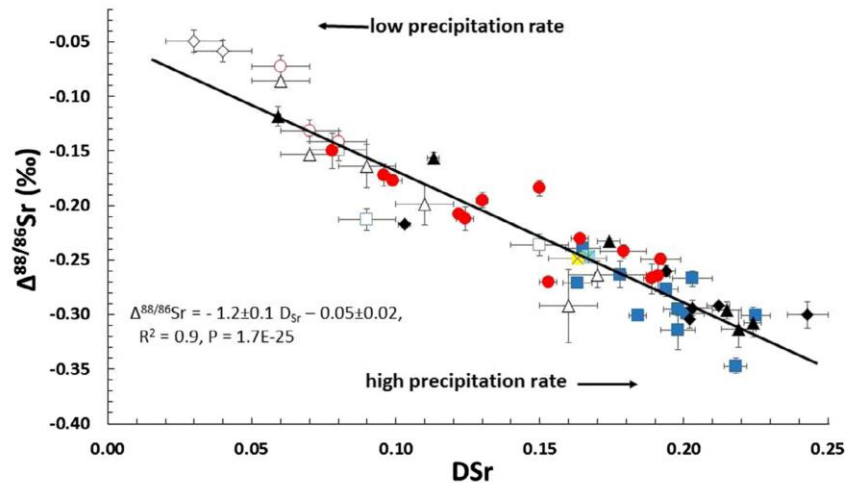
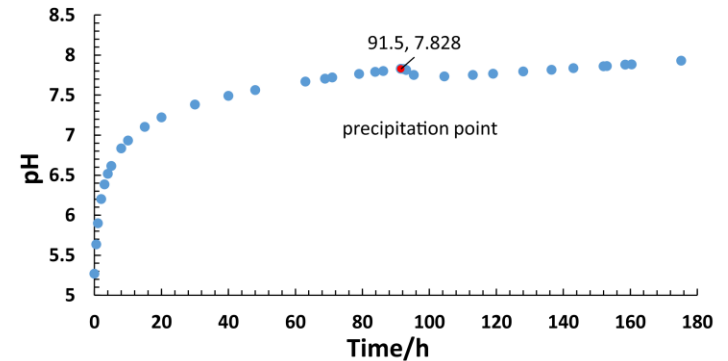
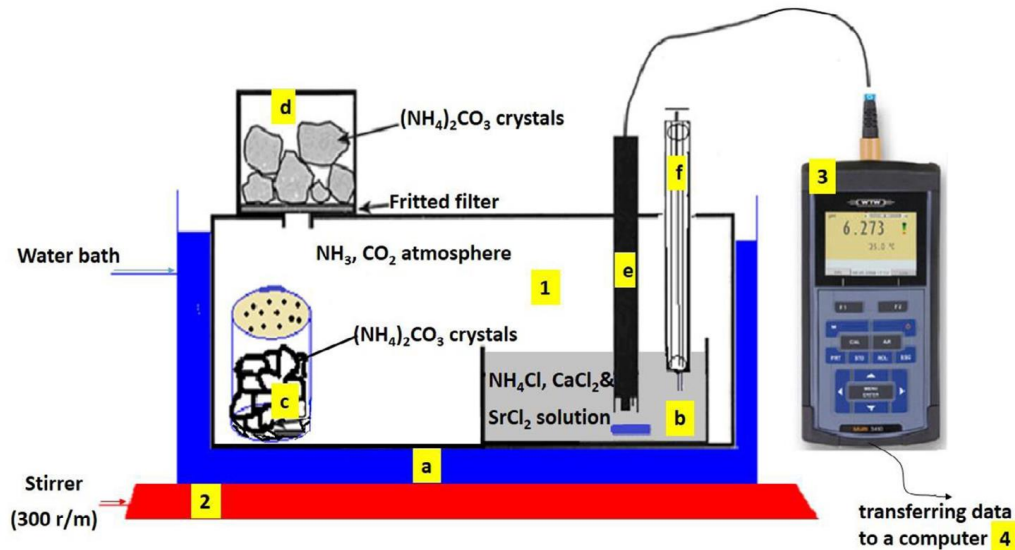
热扩散过程的同位素分馏

活塞式压机的温度曲线

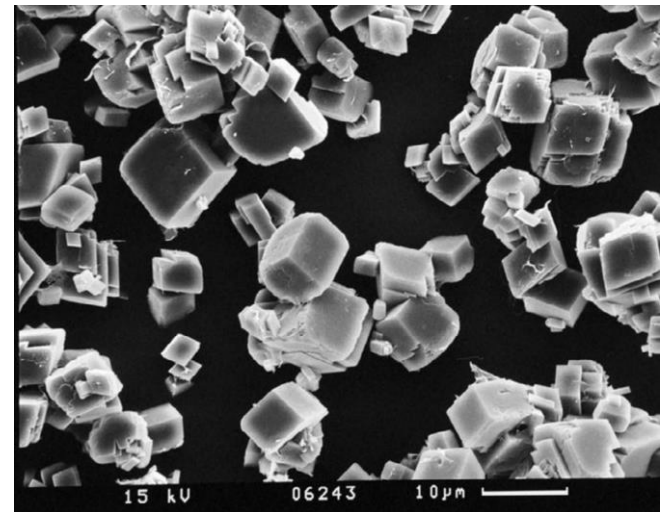


同位素分馏的大小和初始物质组成和体系的总温度无关，只和温度梯度有关。

方解石沉淀过程Sr同位素分馏

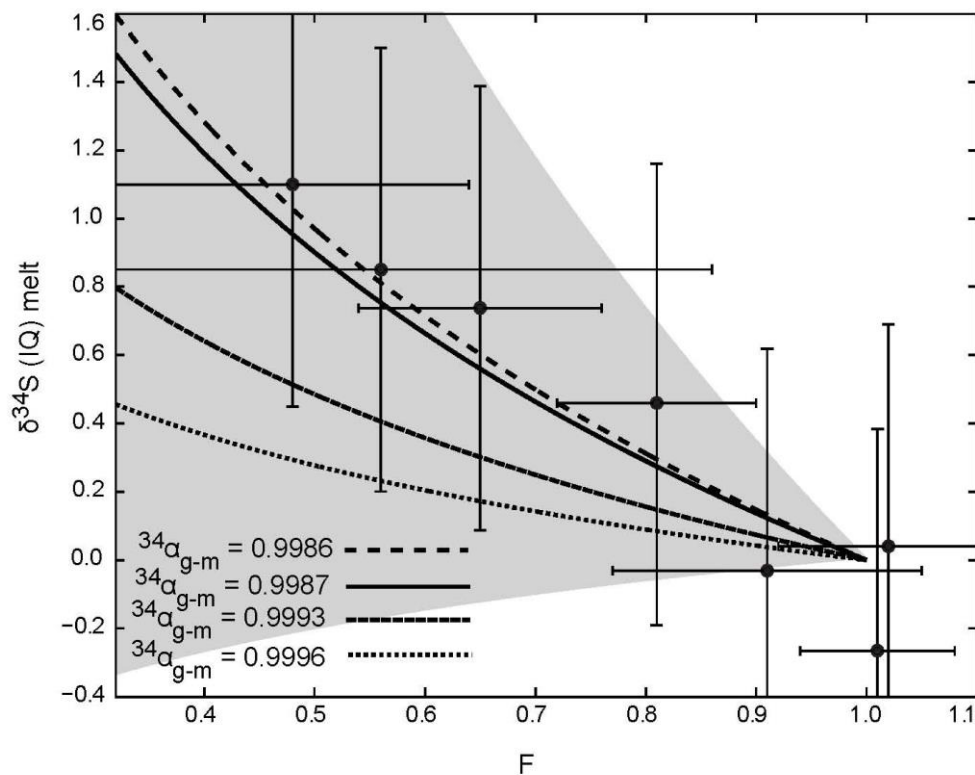
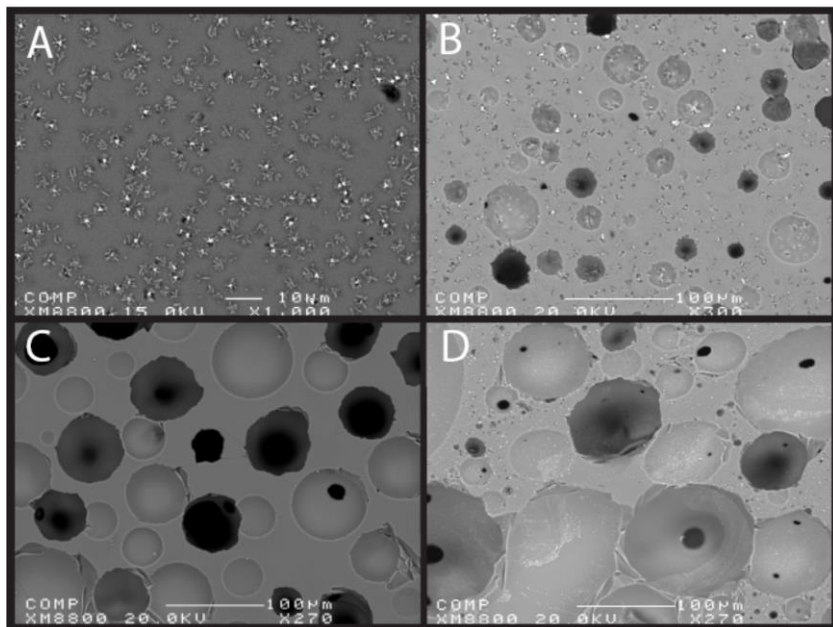


- 5°C, Böhm unpublished
- ▲ 25.0 °C, $[\text{Sr}]/[\text{Ca}]_0 = 0.01$, this study
- △ 25°C, Böhm et al. 2012
- 40°C, Böhm (unpublished)
- *G. ruber*, Böhm et al. 2012
- 12.5 °C, this study; both $[\text{Sr}]/[\text{Ca}]_0$ ratios 0.01 and 0.005
- ◆ 25.0 °C, $[\text{Sr}]/[\text{Ca}]_0 = 0.005$, this study
- 37.5 °C, this study; both $[\text{Sr}]/[\text{Ca}]_0$ ratios 0.01 and 0.005
- ◇ ocean crust, Böhm et al. 2012
- ✕ *G. sacculifer*, Böhm et al. 2012



AlKhatib & Eisenhauer., 2017 GCA

岩浆去气过程S同位素分馏



开放体系中火山气体带走轻S同位素

课程内容

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➤ 矿物-矿物

-变质过程，地幔矿物平衡

➤ 熔体-流体

-流体出溶

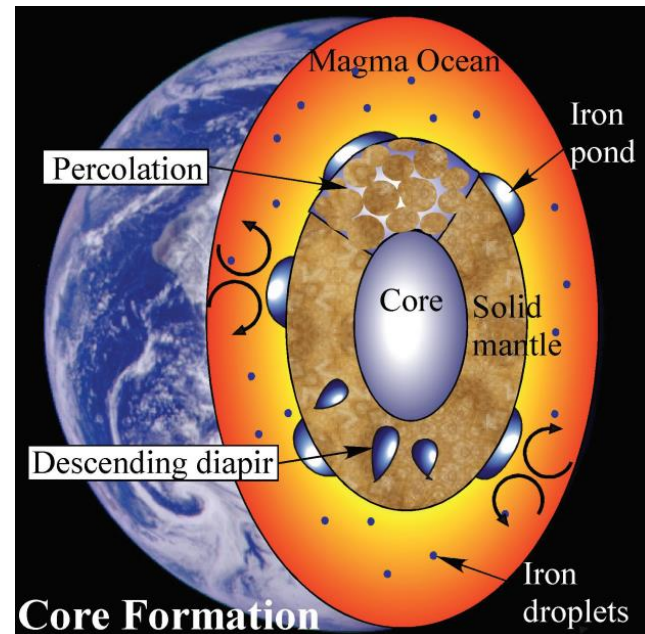
➤ 流体-矿物

-流体中矿物沉淀，结晶

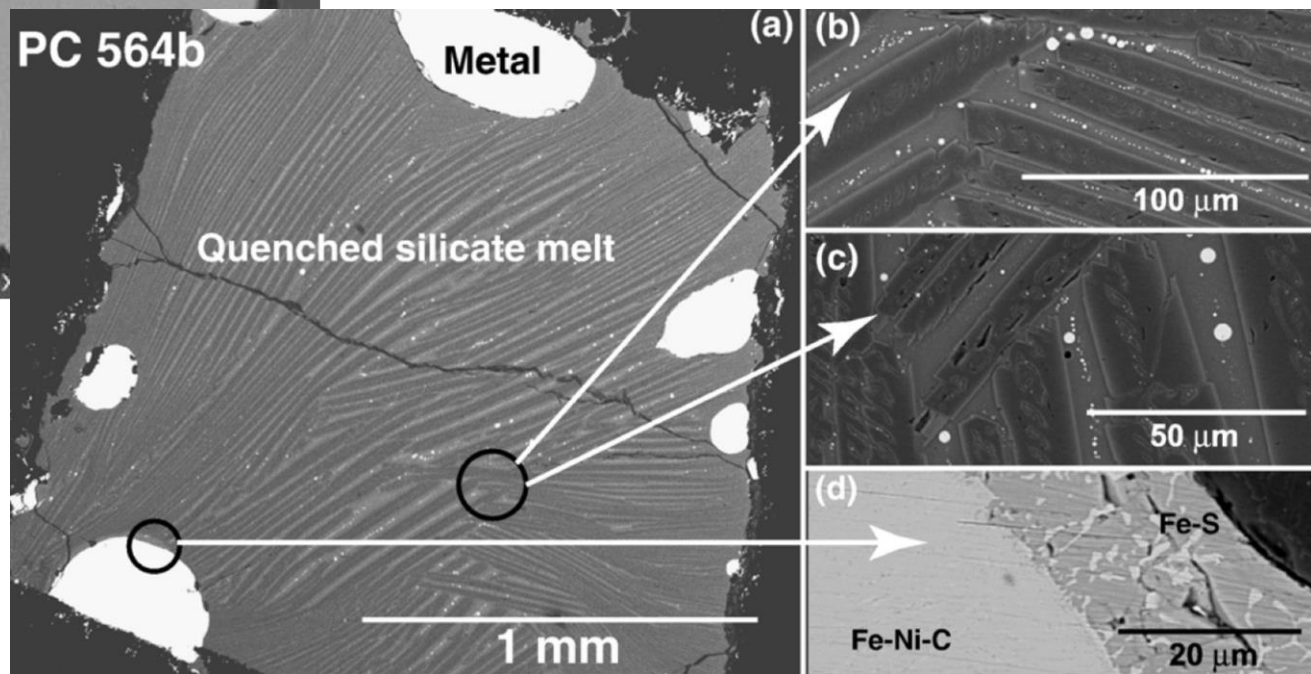
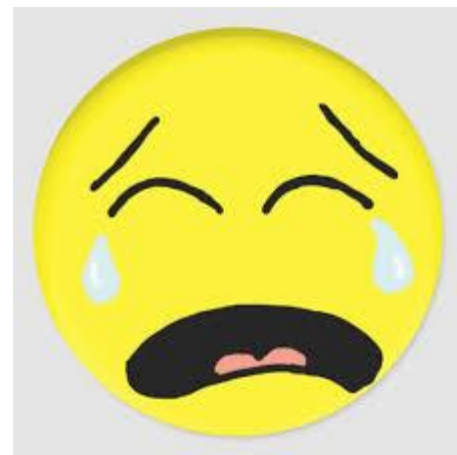
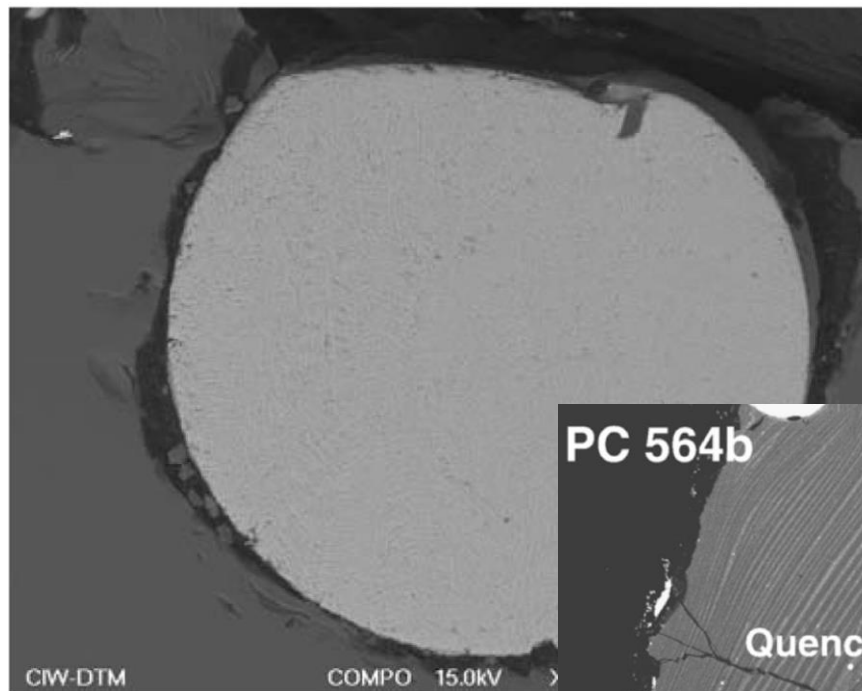
➤ 流体-流体（流体不混融）

-流体沸腾，液态不混溶

两相分离！



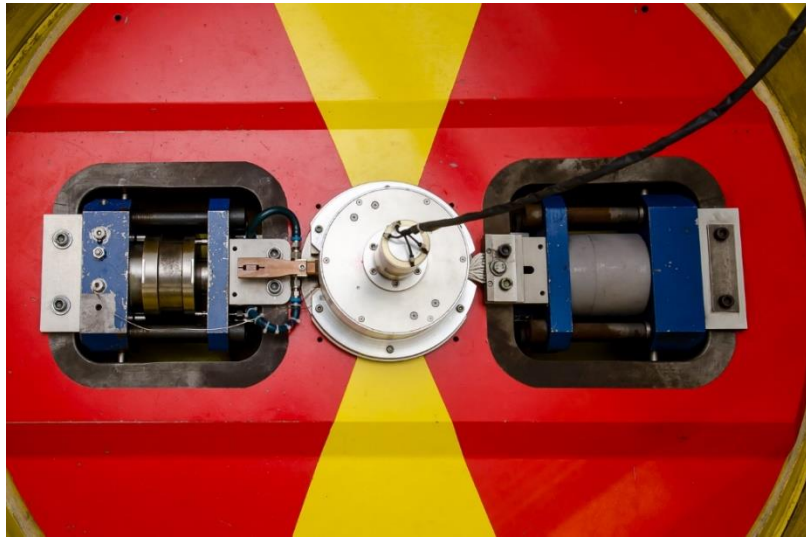
金属熔体和硅酸盐熔体分离



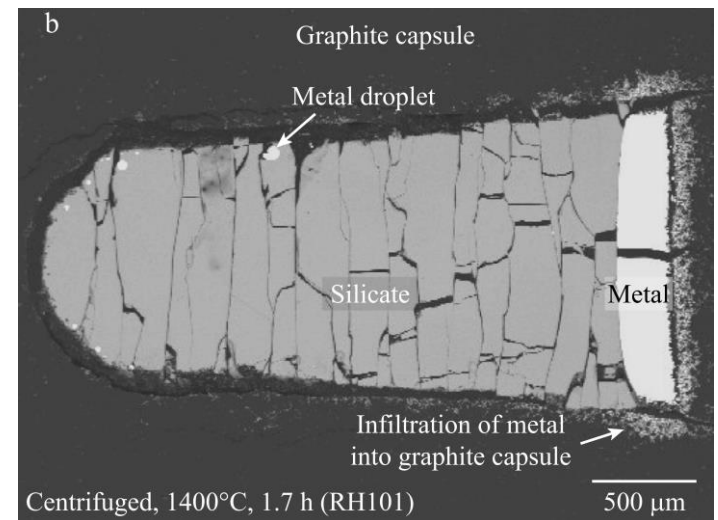
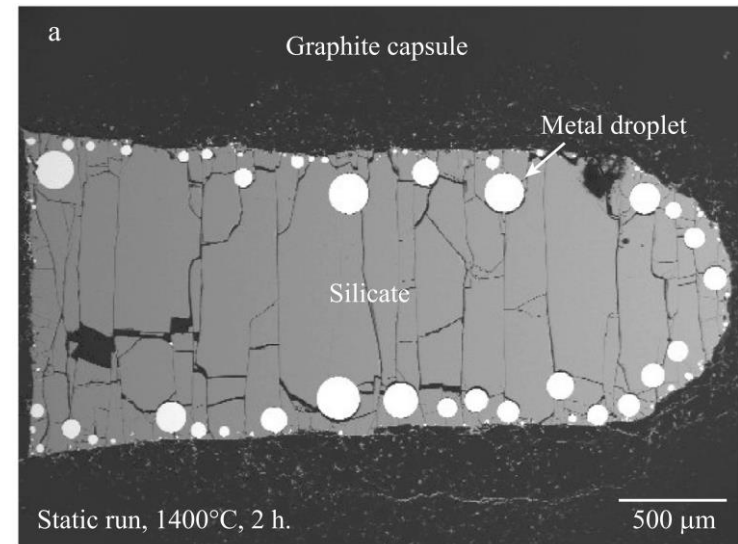
Shahar et al., 2015 GCA

Poitrasson et al., 2009 EPSL

高温高压离心机

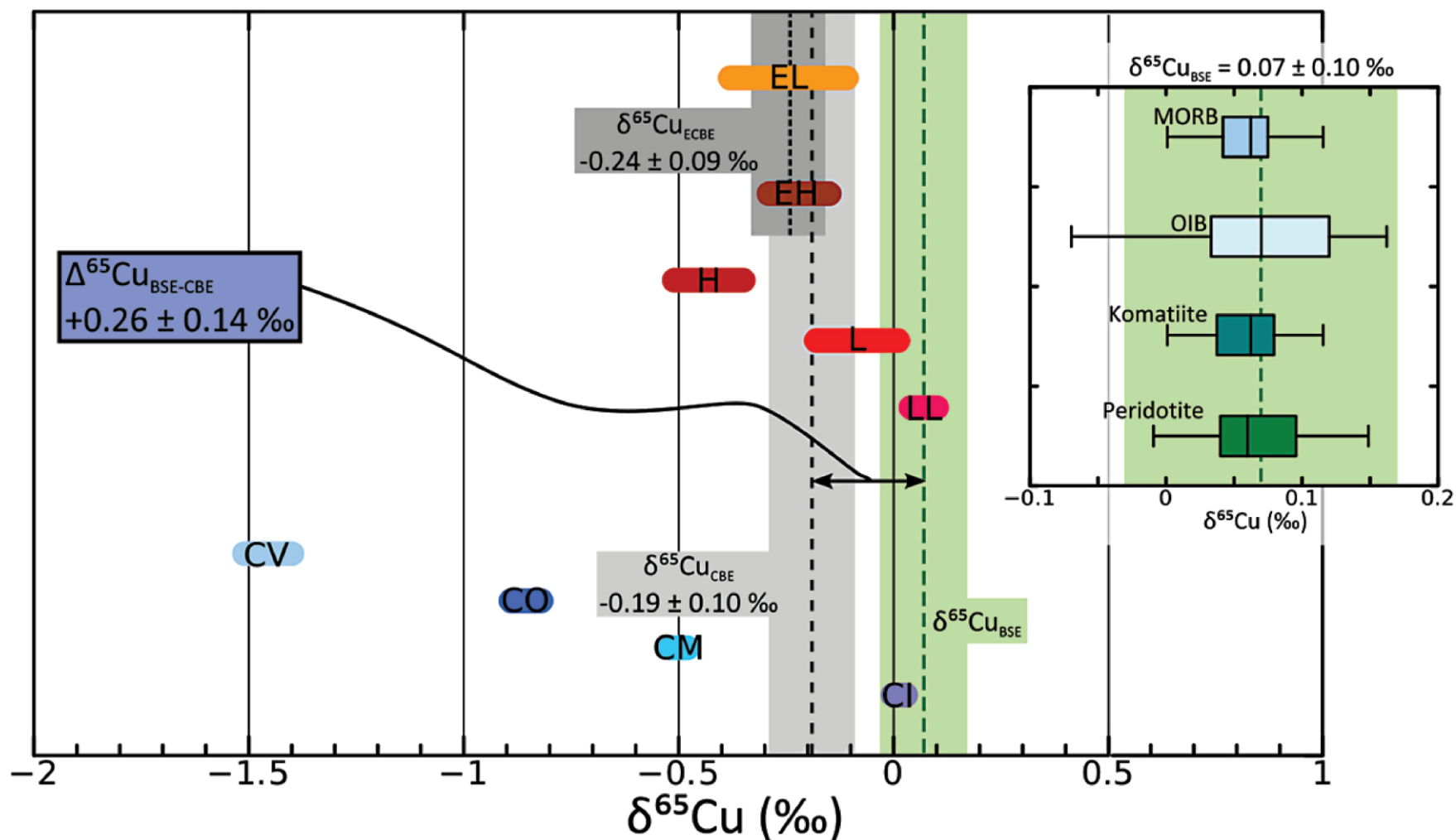


ETH 离心式活塞圆筒压机



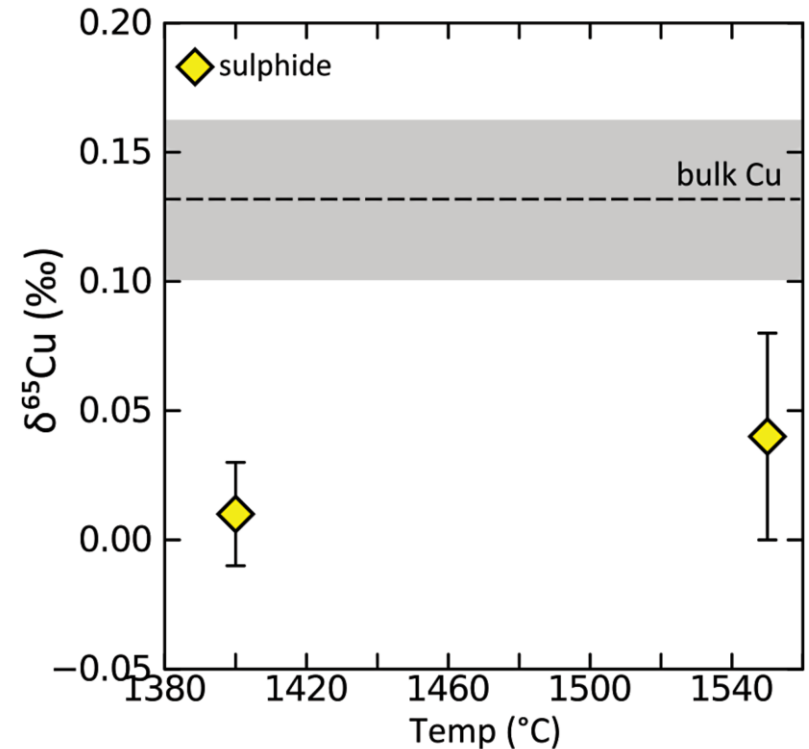
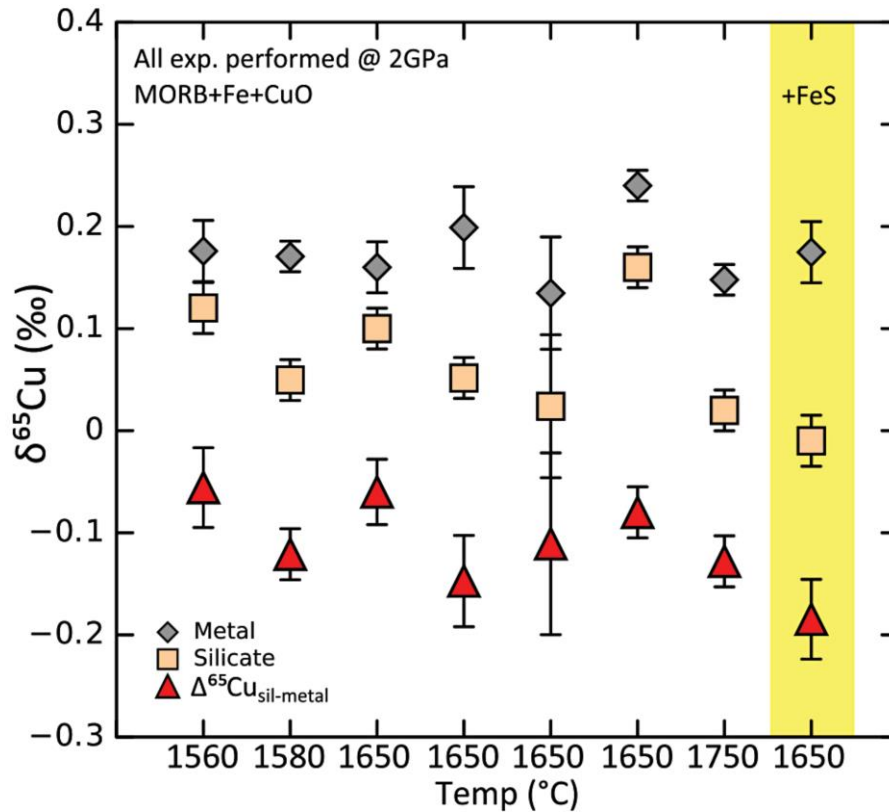
Hin et al., 2013 EPSL

陨石和地球样品的Cu同位素组成

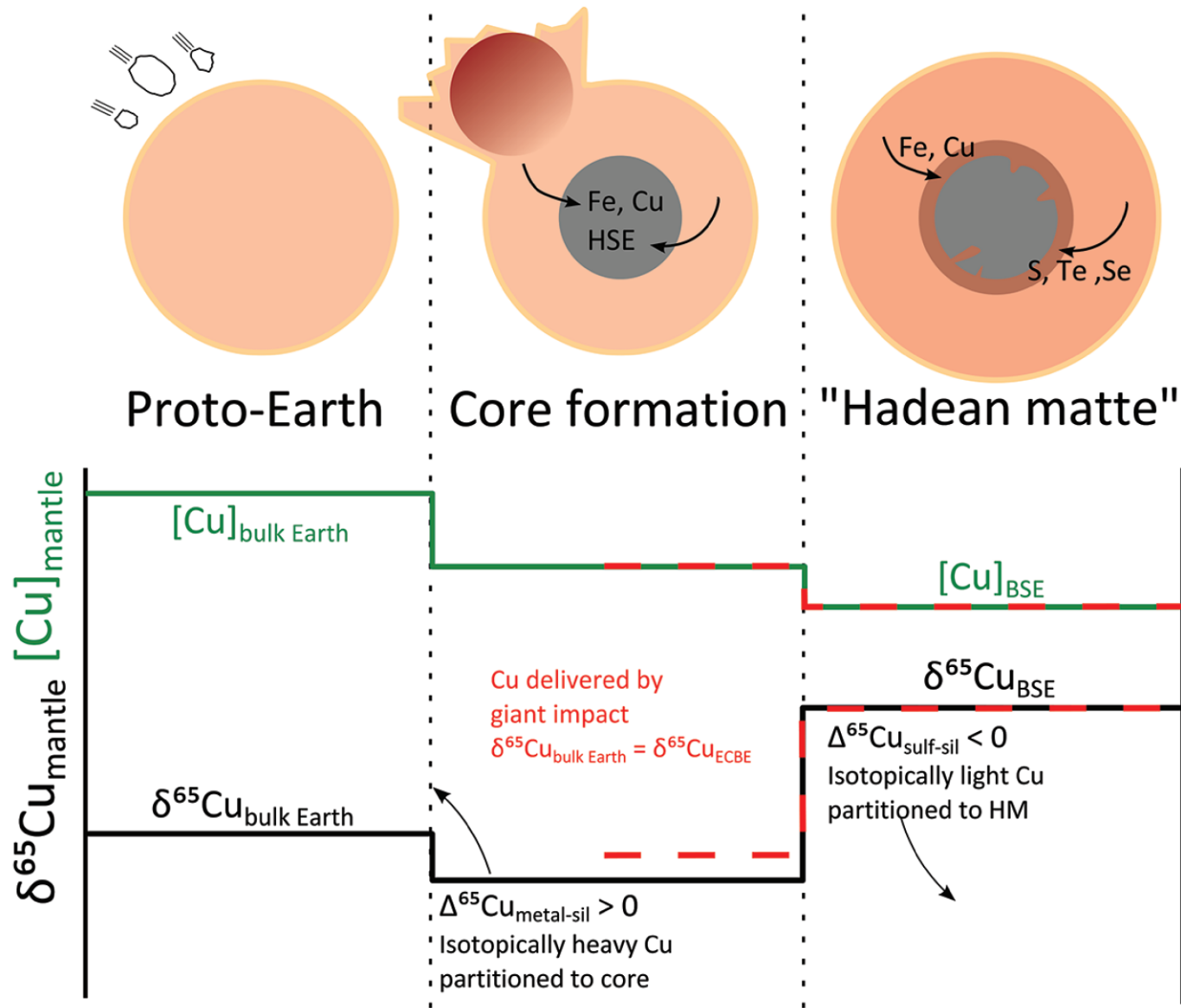


$\delta^{65}\text{Cu}$: 硅酸盐地球 > 陨石

金属、硅酸盐 和 硫化物间Cu同位素分馏



$\delta^{65}\text{Cu}$: 金属 > 硅酸盐 > 硫化物

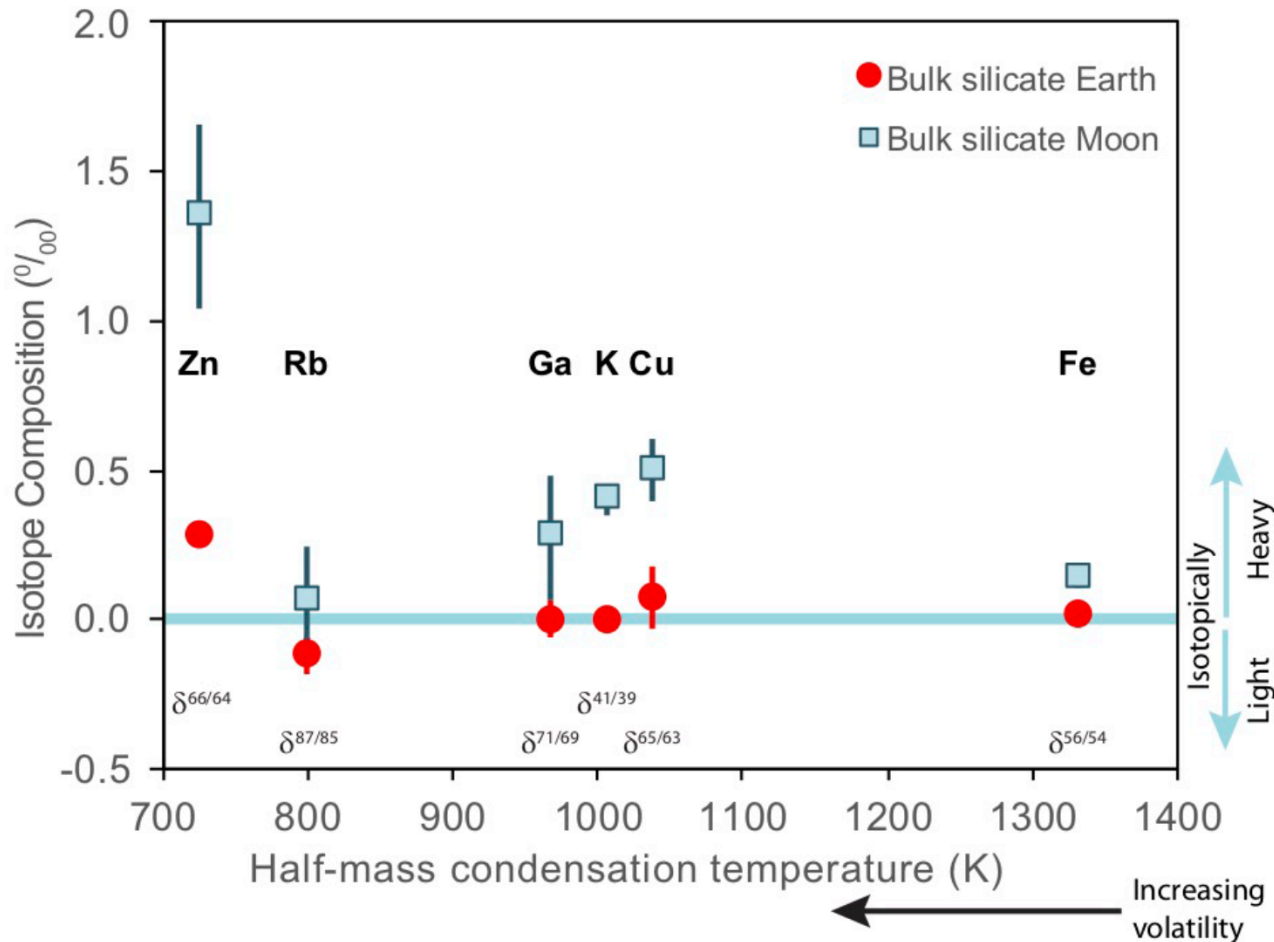


Hadean Matte: 冥古代硫化物沉砂事件

Savage et al., 2015 GPL

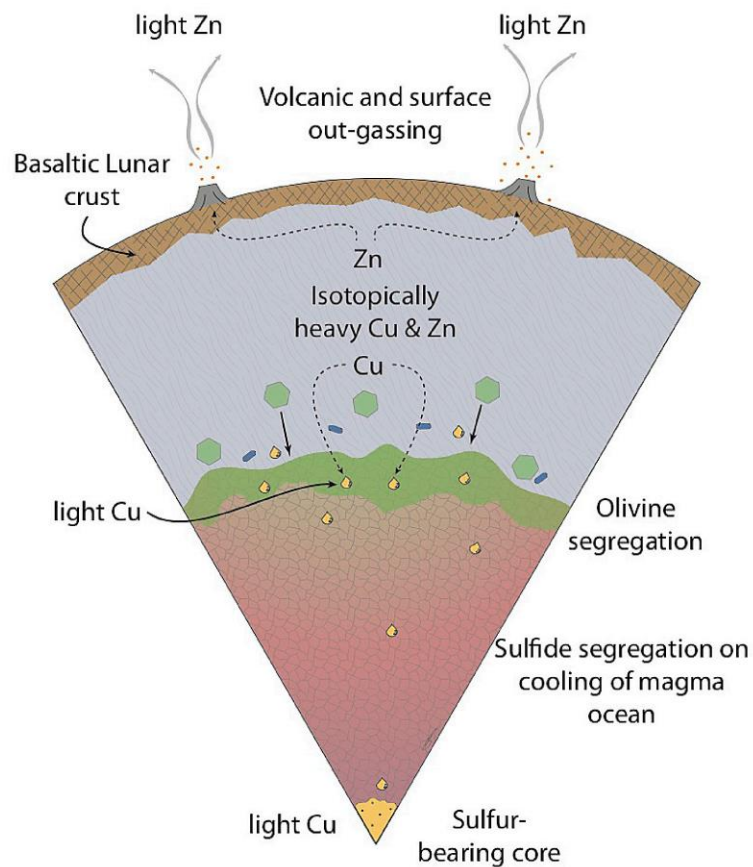
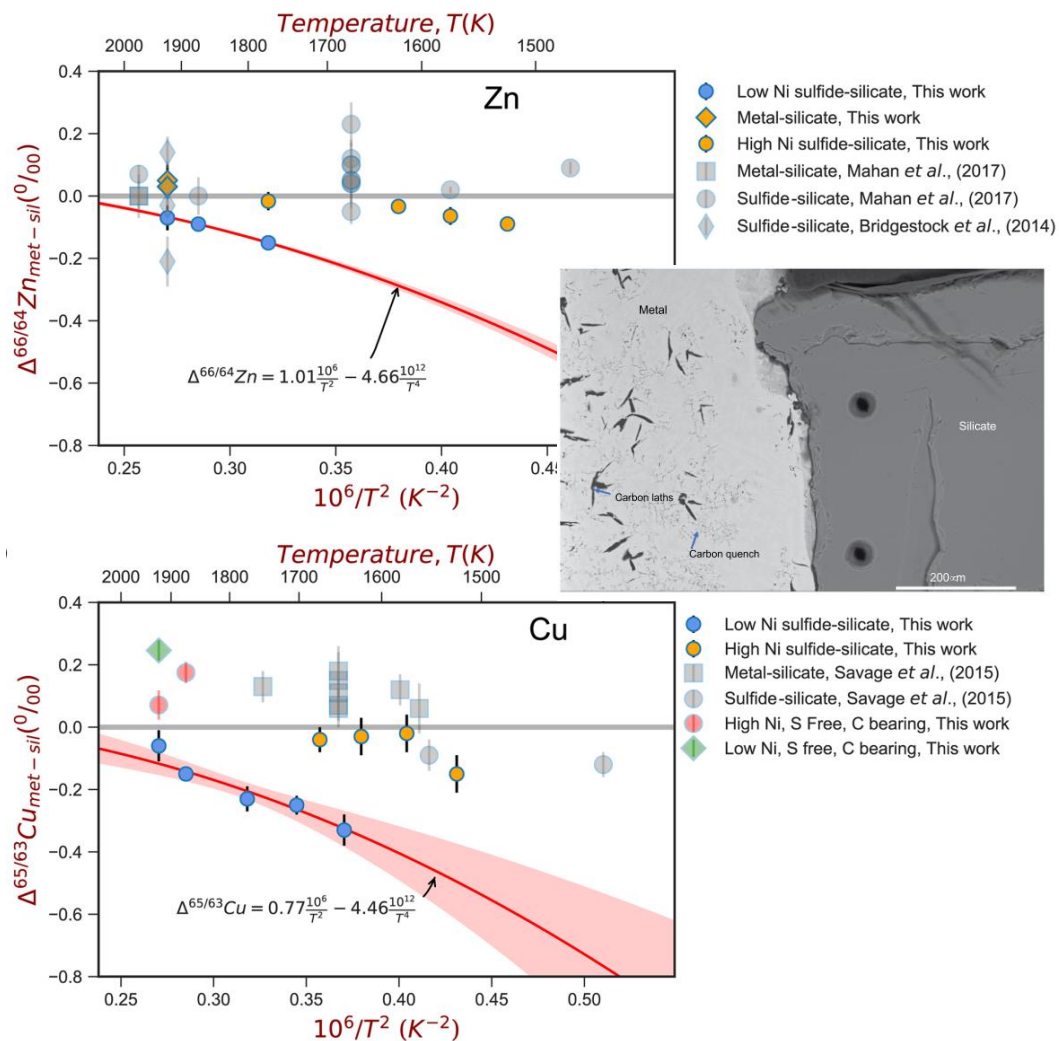
<https://baike.sogou.com/kexue/d49817727078016516.htm?vid=49821212242650886&from=singlemessage>

硅酸盐地球vs. 月球同位素组成



何种原因导致硅酸盐月球同位素偏重：核形成 vs. 岩浆去气？

硅酸盐月球Cu, Zn同位素特征模型



实验测定同位素平衡分馏系数

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➤ 熔体-矿物

-岩浆分异结晶

➤ 矿物-矿物

-变质过程，地幔矿物平衡

➤ 熔体-流体

-流体出溶

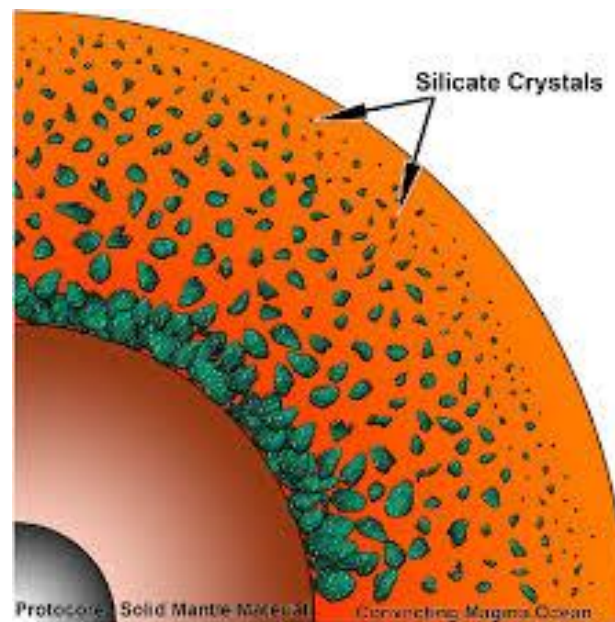
➤ 流体-矿物

-流体中矿物沉淀，结晶

➤ 流体-流体（流体不混融）

-流体沸腾，液态不混溶

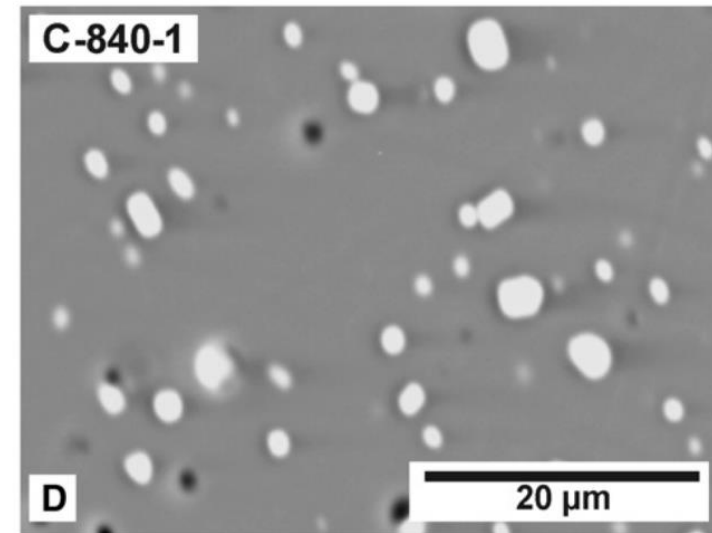
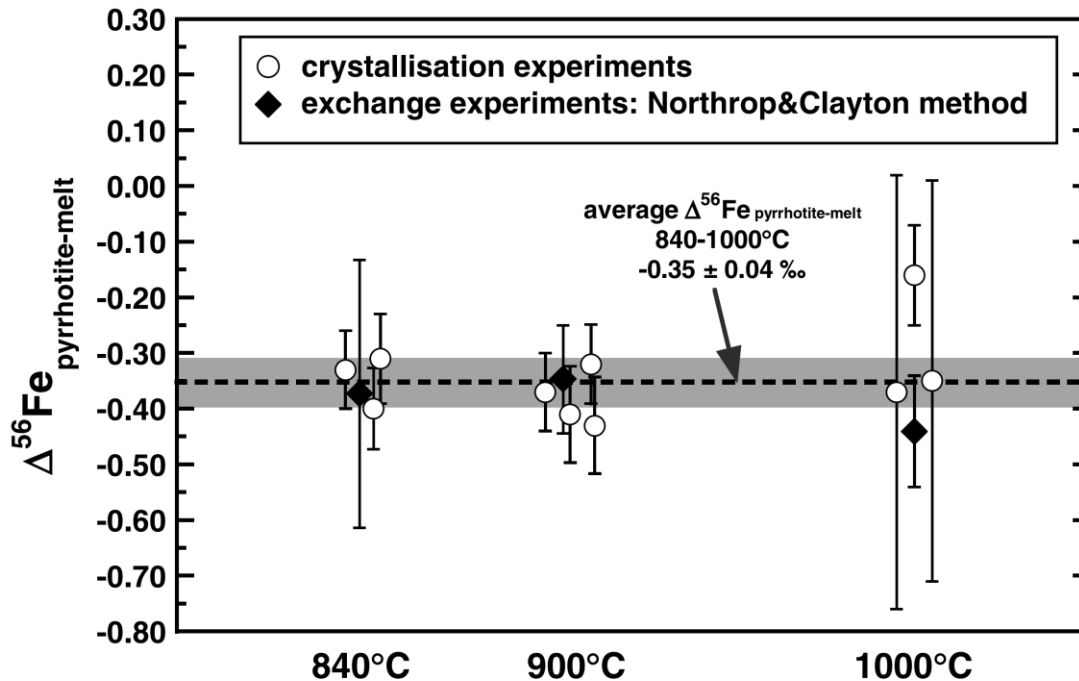
两相分离！



磁黄铁矿和流纹岩熔体间Fe同位素分馏

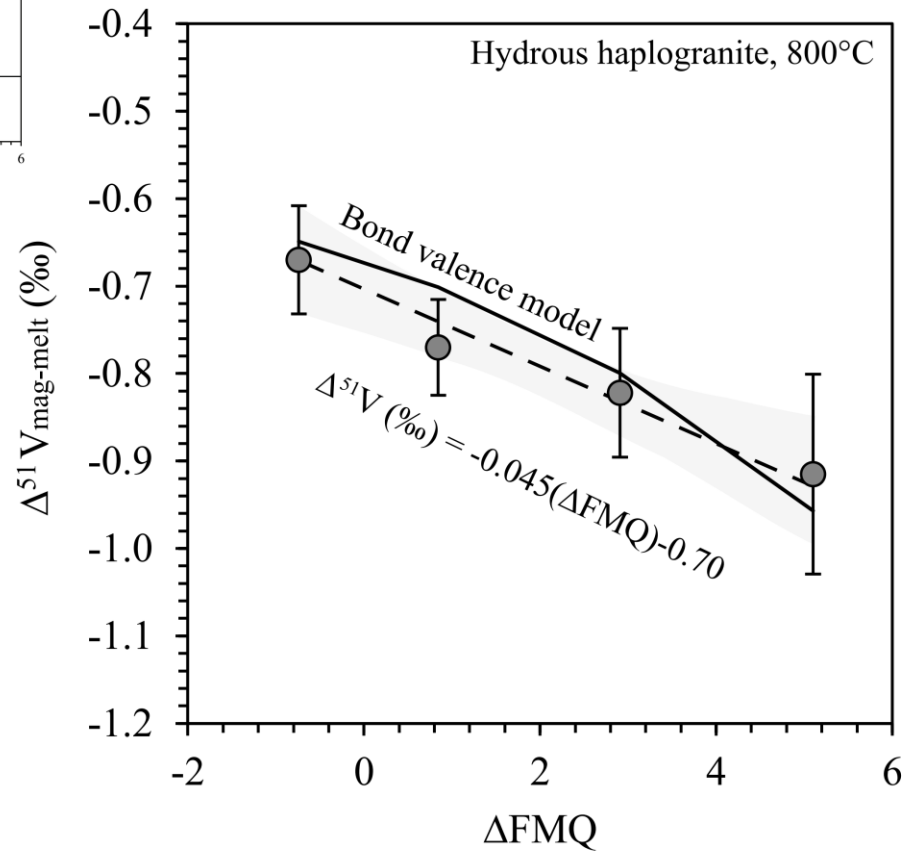
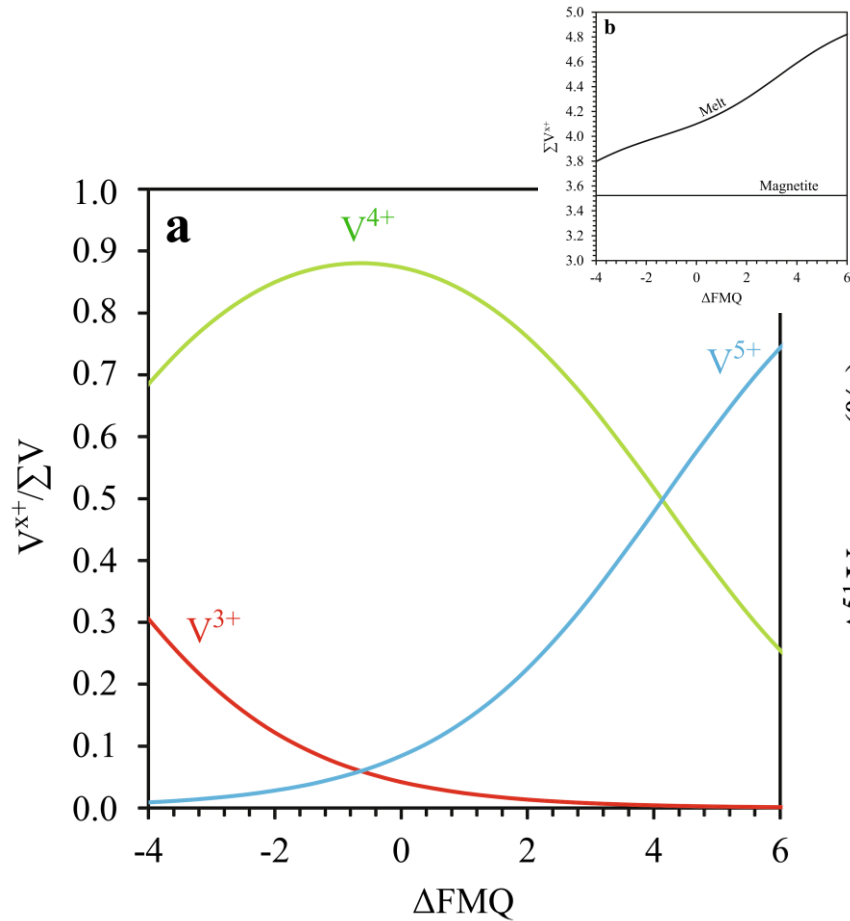
IHPV

500 MPa, 840 and 1000 °C for 120–168 h



磁黄铁矿 Fe^{2+} , 配位数8
熔体 Fe^{2+} 和 Fe^{3+} , 配位数4 (5或6)

磁铁矿和熔体间V同位素分馏



$$\Delta^{51}V_{\text{Mag-Melt}} (\text{‰}) = -0.045 \pm 0.021(\Delta FMQ) - 0.70 \pm 0.05.$$

实验测定同位素平衡分馏系数

➤ 熔体-熔体 (金属, 硅酸盐, 硫化物...)

-核幔分异, 岩浆演化熔体不混融

➤ 熔体-矿物

-岩浆分异结晶

➤ 矿物-矿物

-岩浆变质过程, 地幔矿物平衡

➤ 熔体-流体

-流体出溶

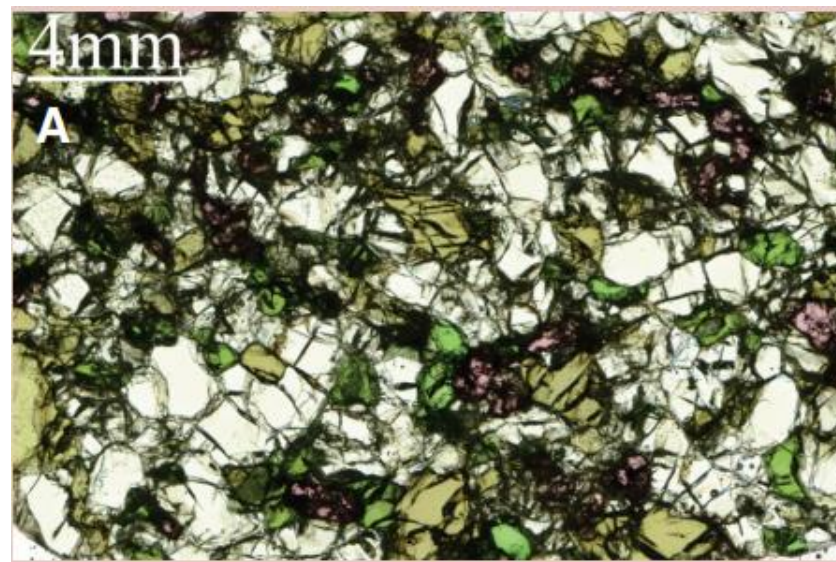
➤ 流体-矿物

-流体中矿物沉淀, 结晶

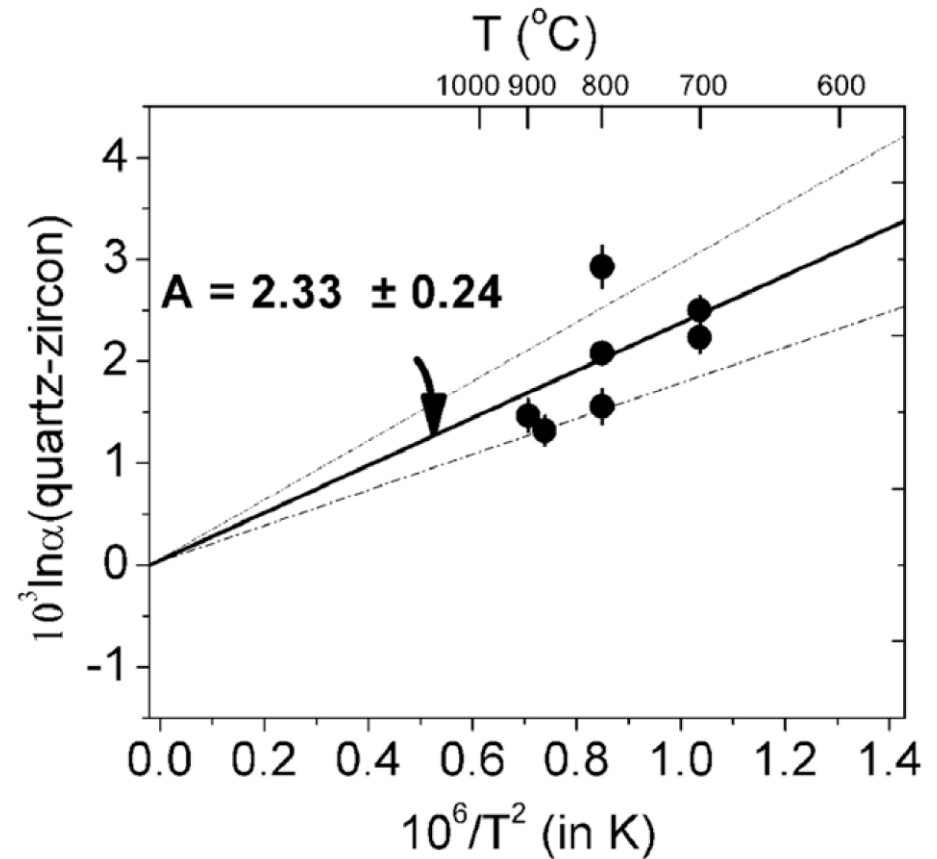
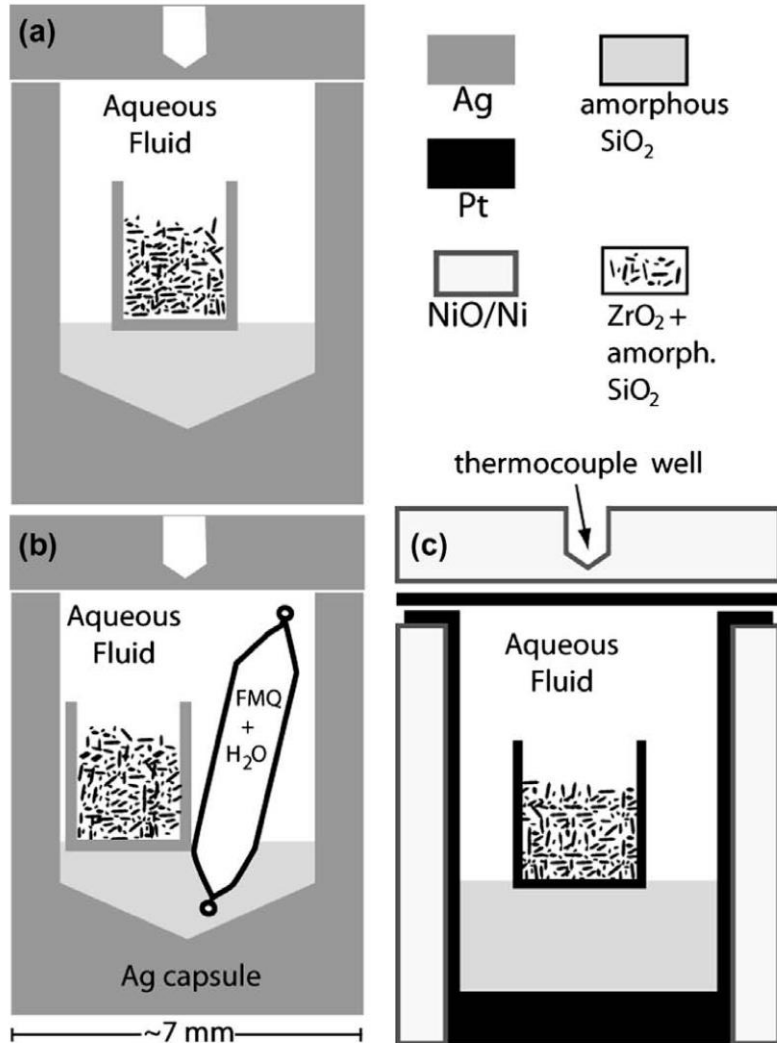
➤ 流体-流体 (流体不混融)

-流体沸腾, 液态不混溶

两相分离!

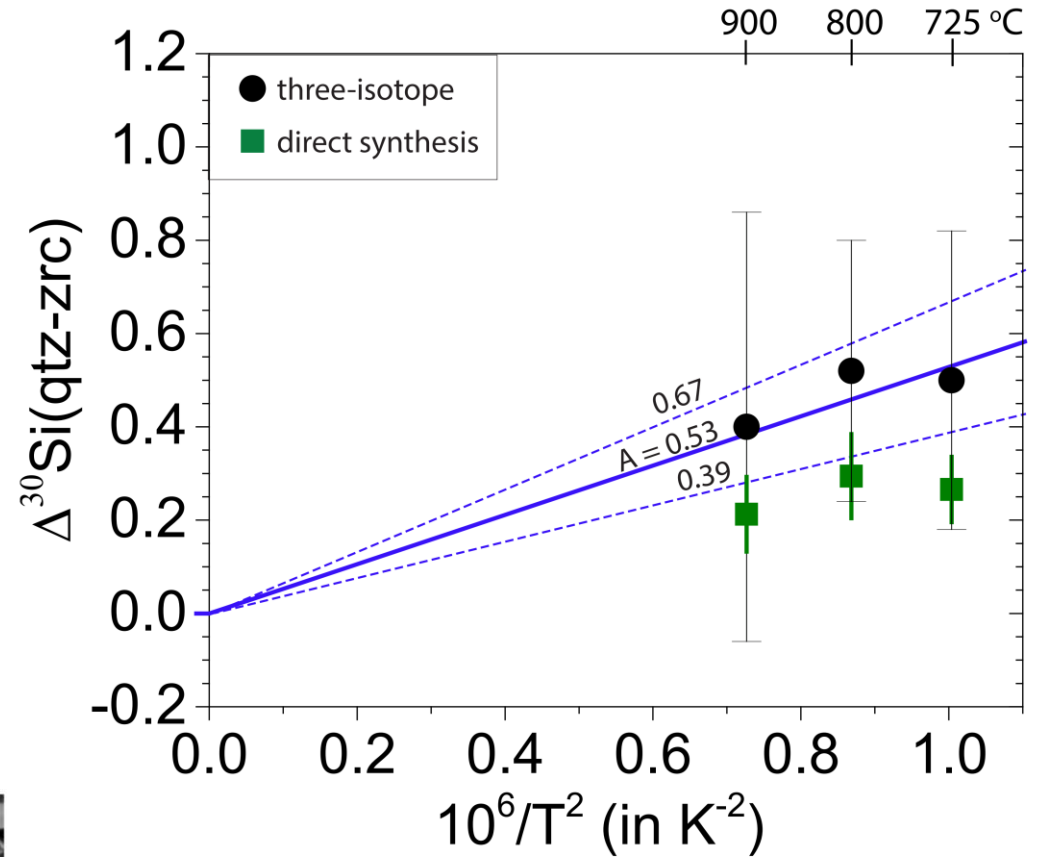
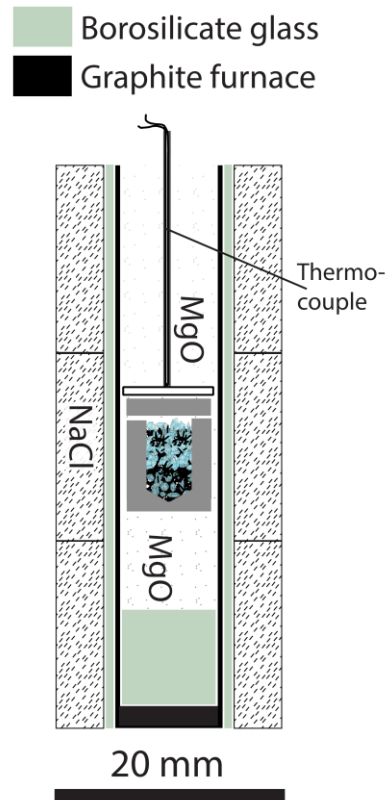


石英和锆石间O同位素分馏



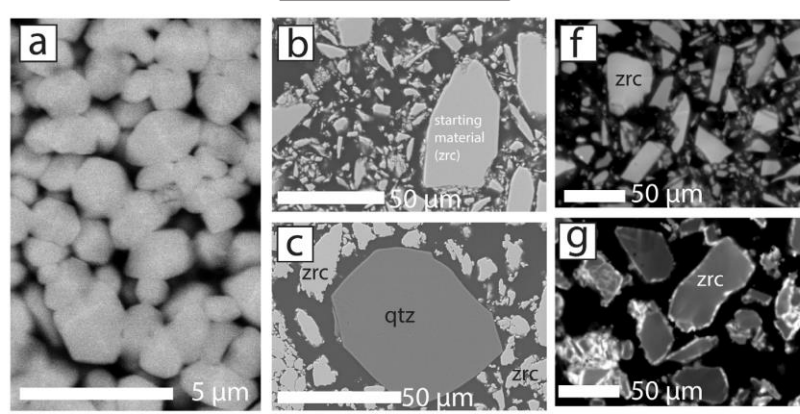
$$1000 \ln \alpha_{\text{qtz-zrc}} = (2.33 \pm 0.24) \times 10^6/T^2(\text{in K})$$

石英和锆石间si同位素分馏



$$\Delta^{30}\text{Si}(\text{qtz-zrc}) = (0.53 \pm 0.14) \times 10^6/\text{T}^2$$

Trail et al., 2019 GCA



实验测定同位素平衡分馏系数

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➤ 熔体-矿物

-岩浆结晶分异

➤ 矿物-矿物

-变质过程，地幔矿物平衡

➤ 熔体-流体

-流体出溶，岩浆热液

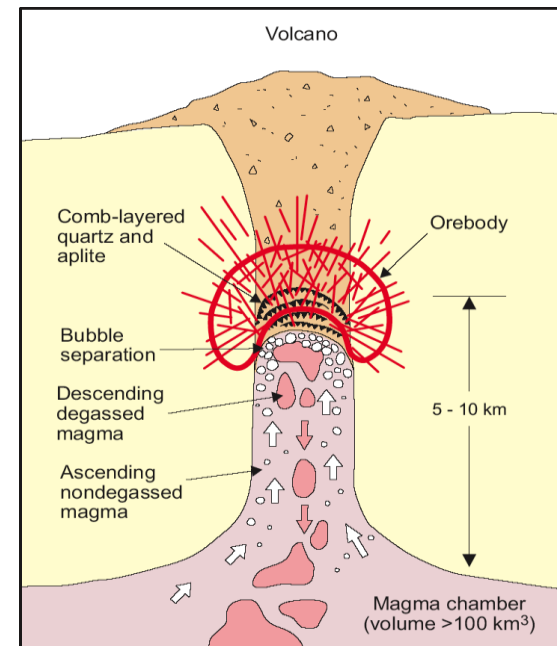
➤ 流体-矿物

-流体中矿物沉淀，结晶

➤ 流体-流体（流体不混溶）

-流体沸腾，液态不混溶

两相分离！



Sinclair (2007)

岩浆房中的流体作用

trigger volcanic eruptions



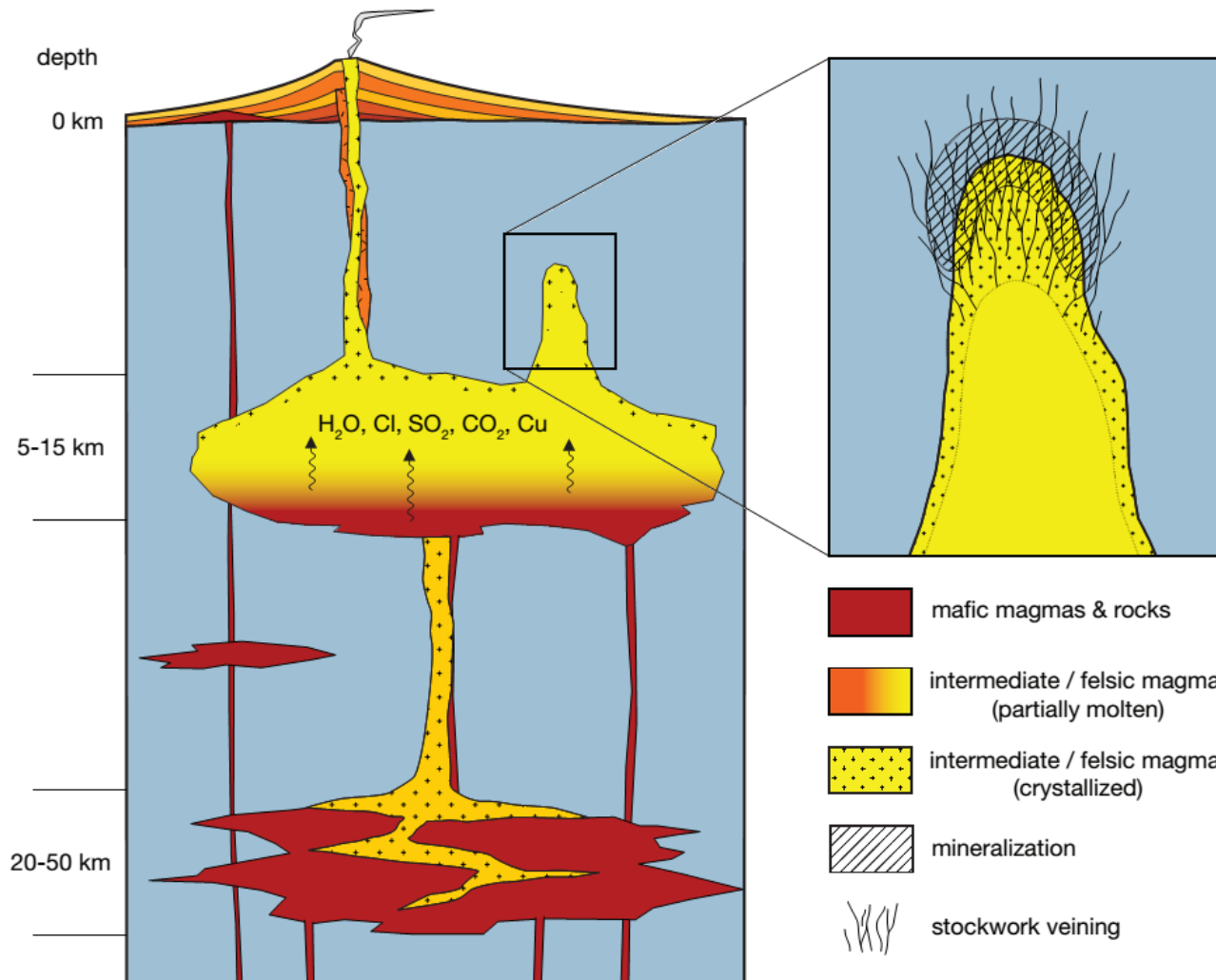
form ore deposits



St Helens



岩浆房和斑岩型矿床



斑岩型矿床的经济价值

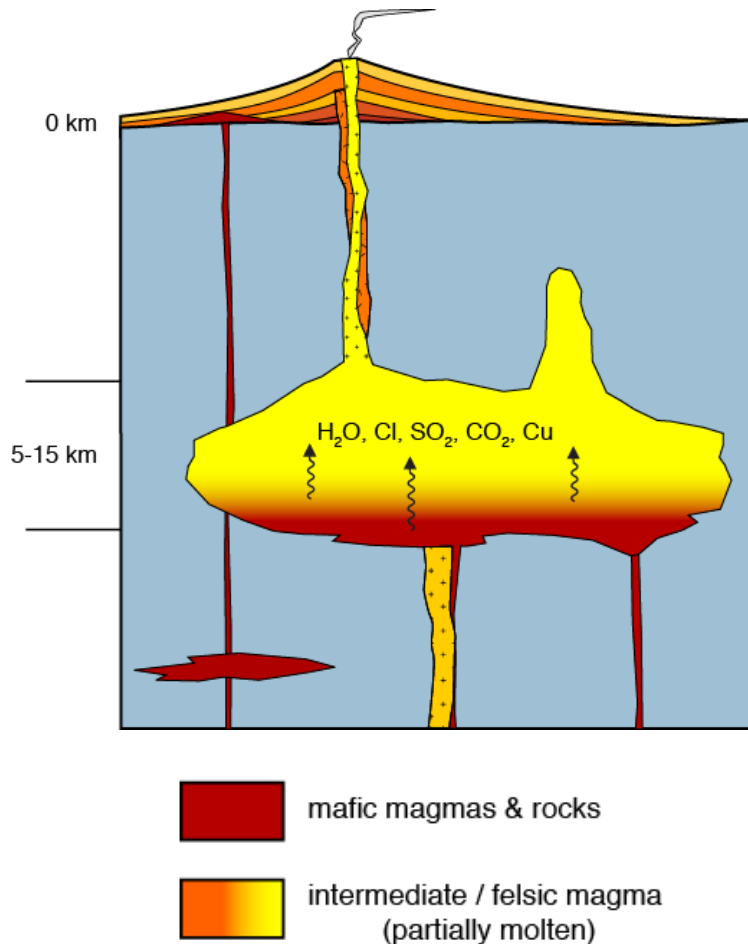


Bingham Canyon, UT

	Price \$/kg	values
2.9E+10 kg Cu	5.87	170,000,000,000 \$
1.7E+09 kg Mo	28.7	49,000,000,000 \$
1.2E+06 kg Au	39,200	47,000,000,000 \$
1.7E+07 kg Ag	511	8,700,000,000 \$

270,000,000,000 \$

Volatile fluxing



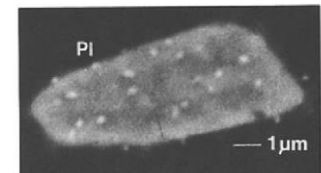
modified from Audétat and Simon (2013)

‘volatiles fluxing’证据

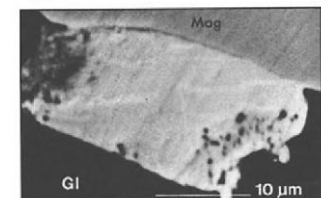
- 火山气体中高含量的挥发分和金属元素
- 酸性岩浆岩中硫化物中高的 Cu, Se, Te 和 Cd 含量
- 熔体包裹体和矿物中异常高的 Li/Cu 含量



Fumarole



A

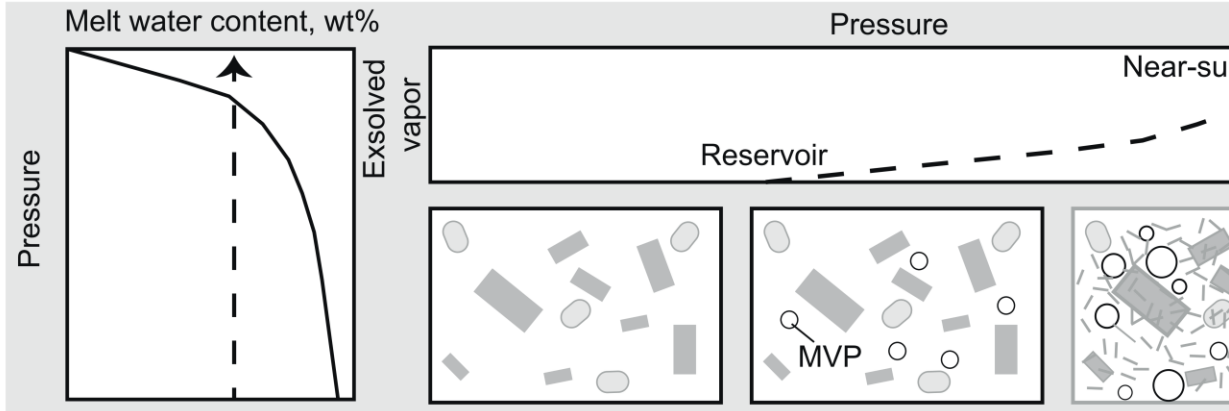


B

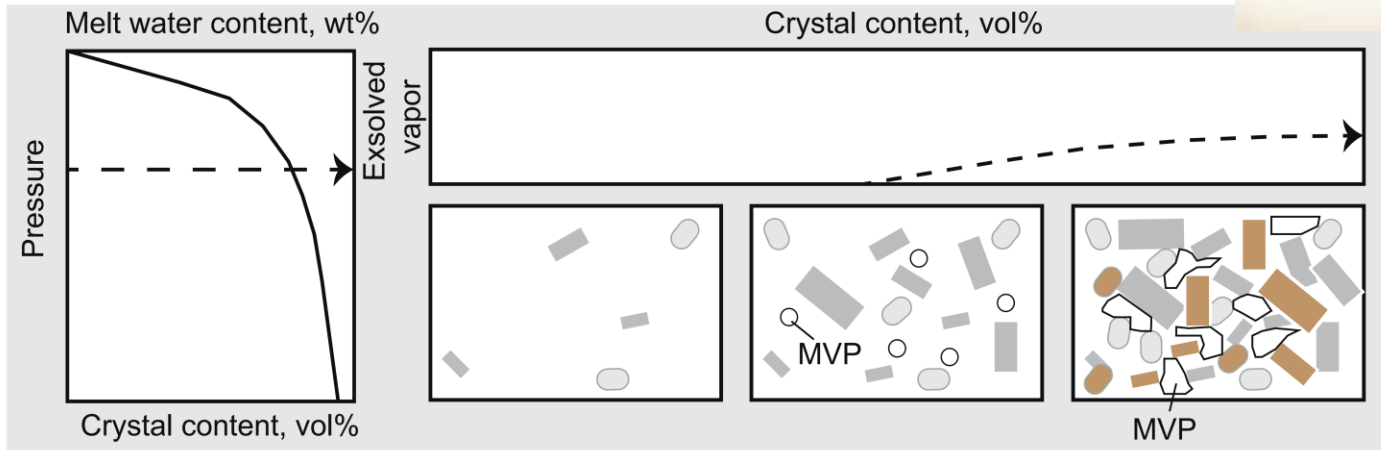
Sulphide in Mount Pinatubo, Philippines (Hattori 1993, 1996)

岩浆中挥发分饱和和

A: Exsolution of volatiles during decompression, “first boiling”

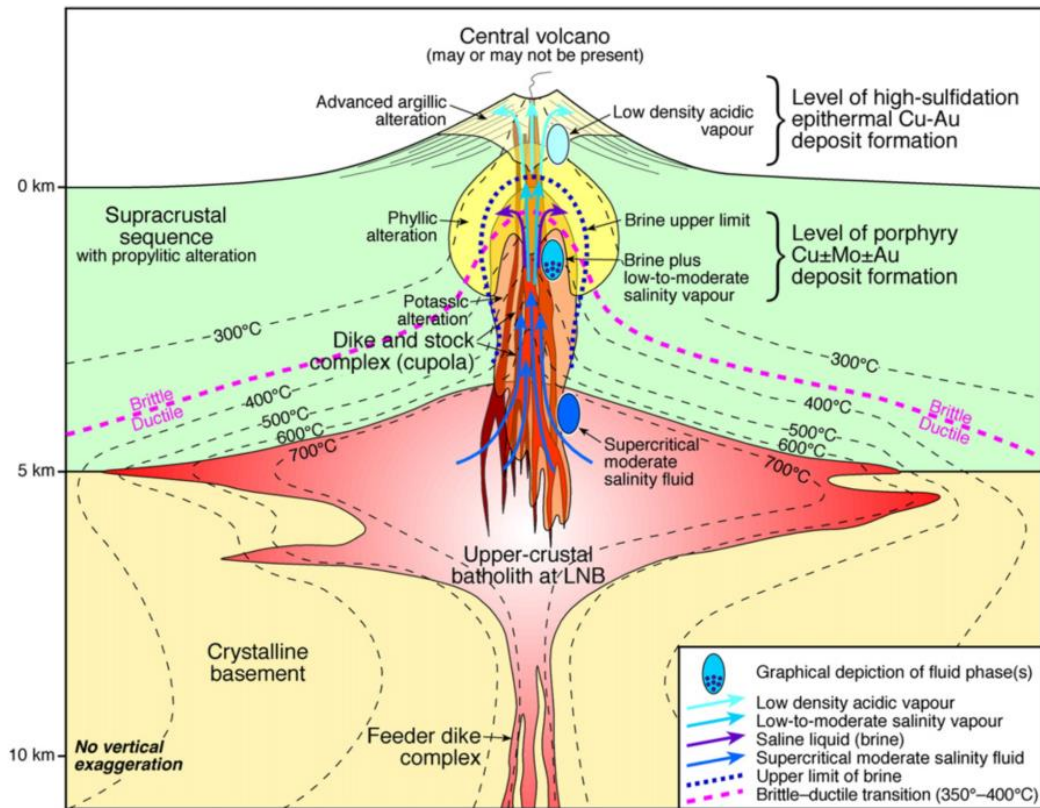


B: Exsolution of volatiles during cooling and crystallisation, “second boiling”

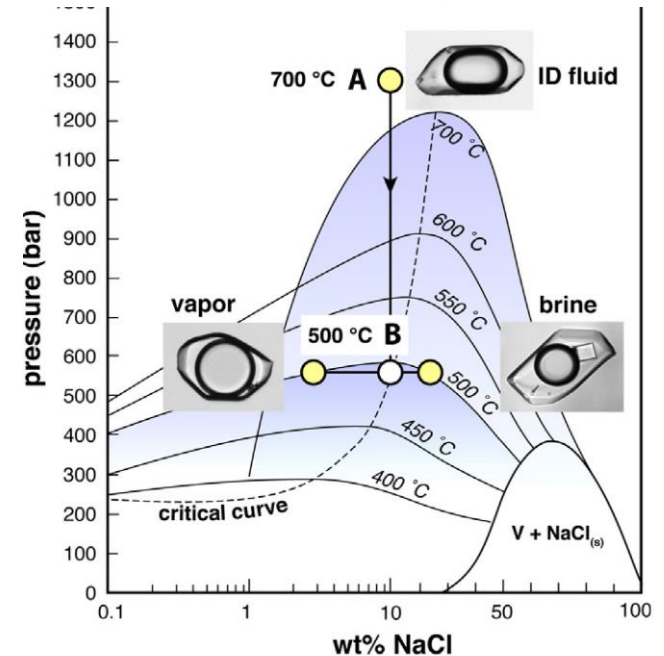
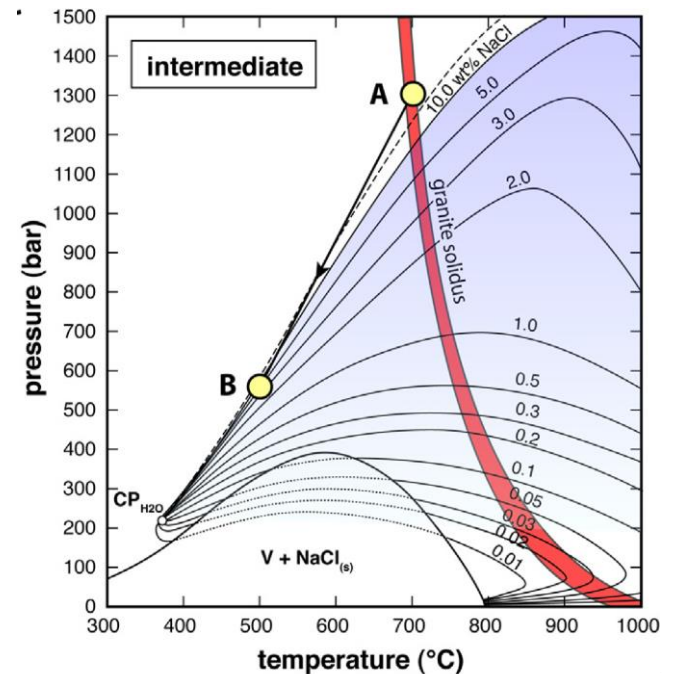


斑岩系统中的流体

Single phase fluid → Brine
→ Vapor



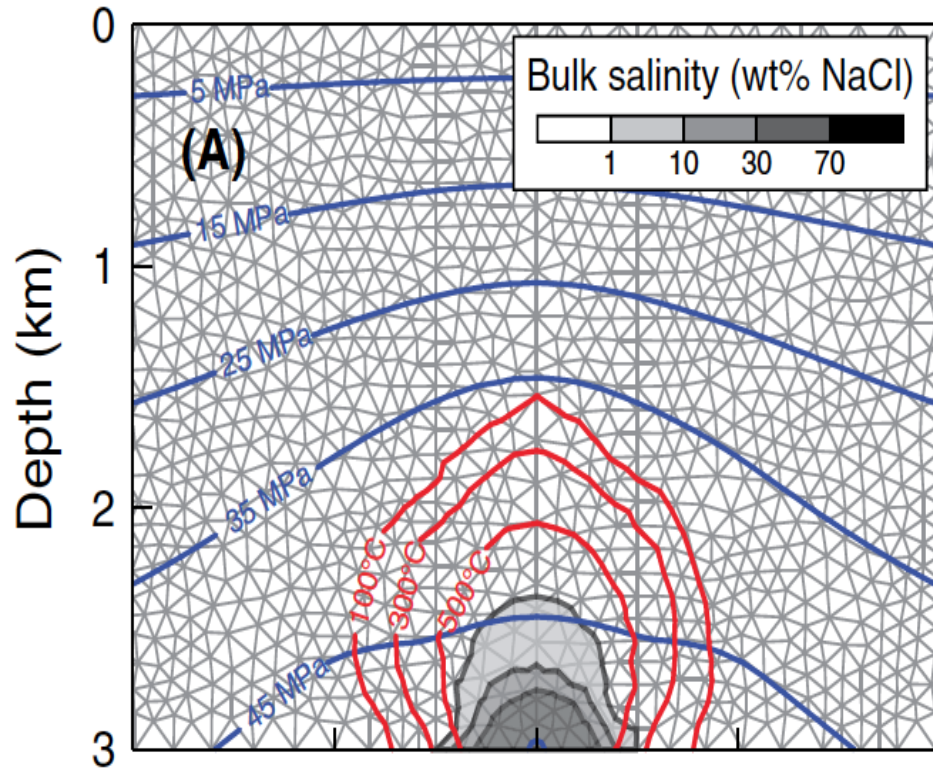
Richard, 2011 OGR



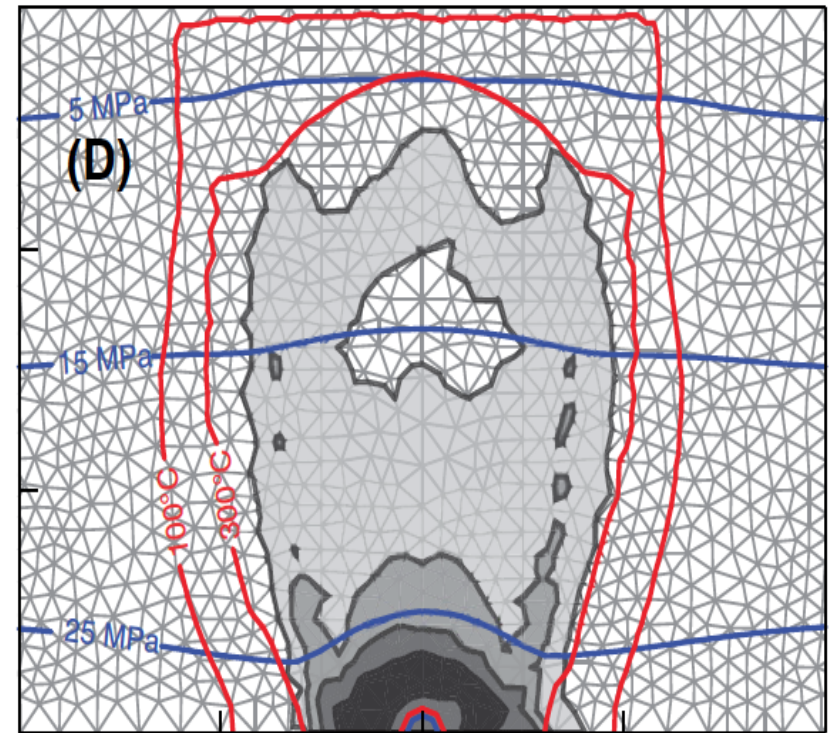
Audetat & Li., 2017 OGR

数值模拟流体在岩浆房中运移

500 年

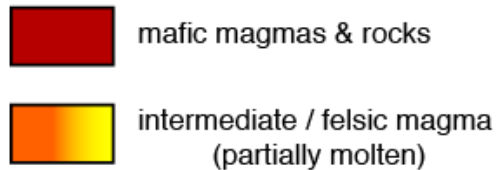
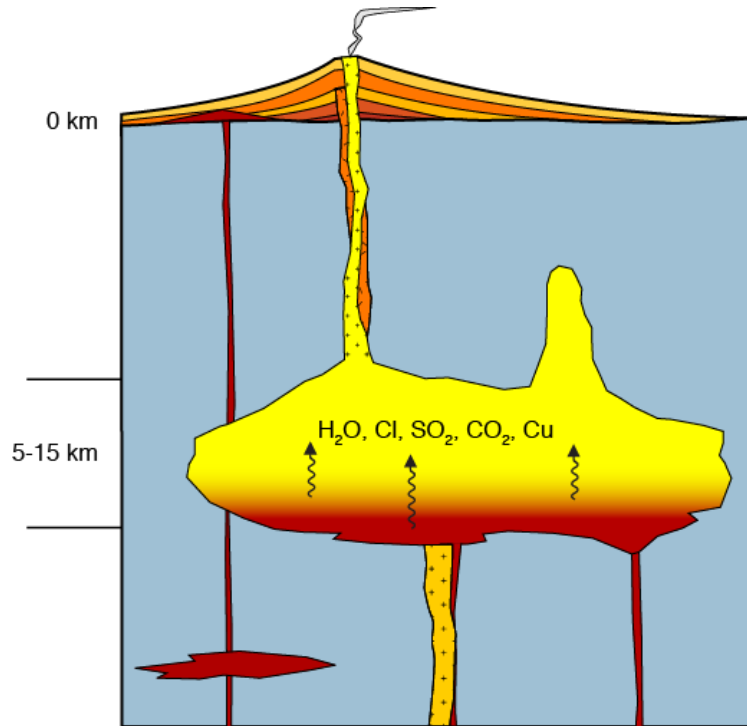


2000 年



高密度brine 积累在深部，低密度vapor运移到浅部

Volatile fluxing中的问题



□ 基性岩浆出溶的流体成分是什么？挥发性元素（S, Cl）和金属？

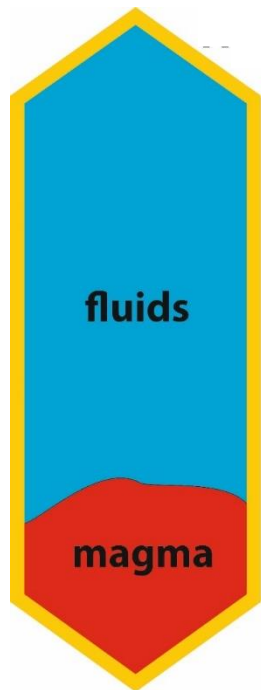
□ 这些出溶的流体对上地壳的酸性岩浆房的影响？

□ 出溶的流体后期的演化？

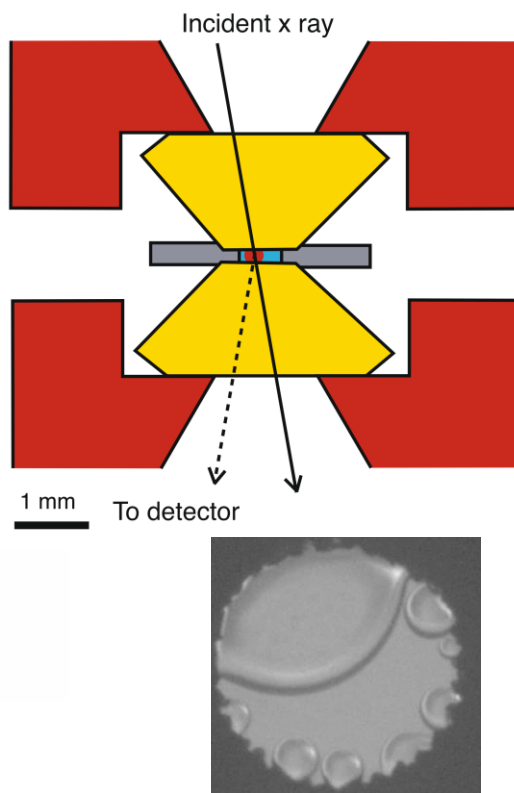
Brine/vapor的地球化学特征？

实验研究流体-熔体分配系数方法

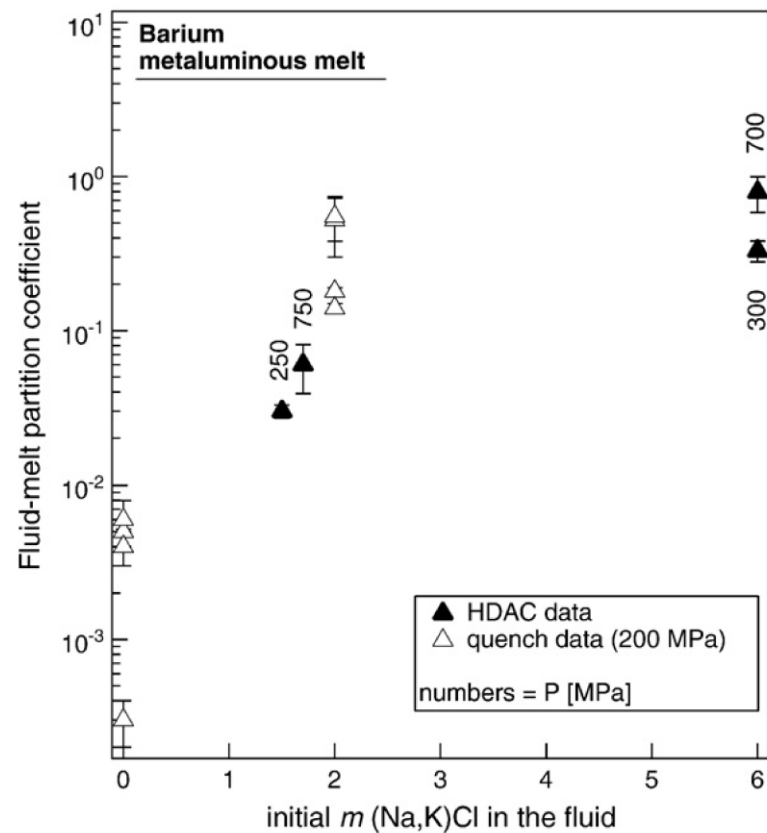
1. 淬火分析法



2. 原位分析法



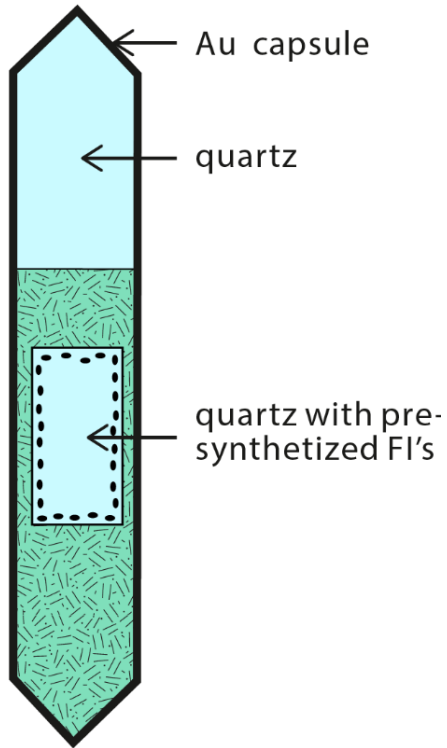
Kawamoto et al., 2014 EPS



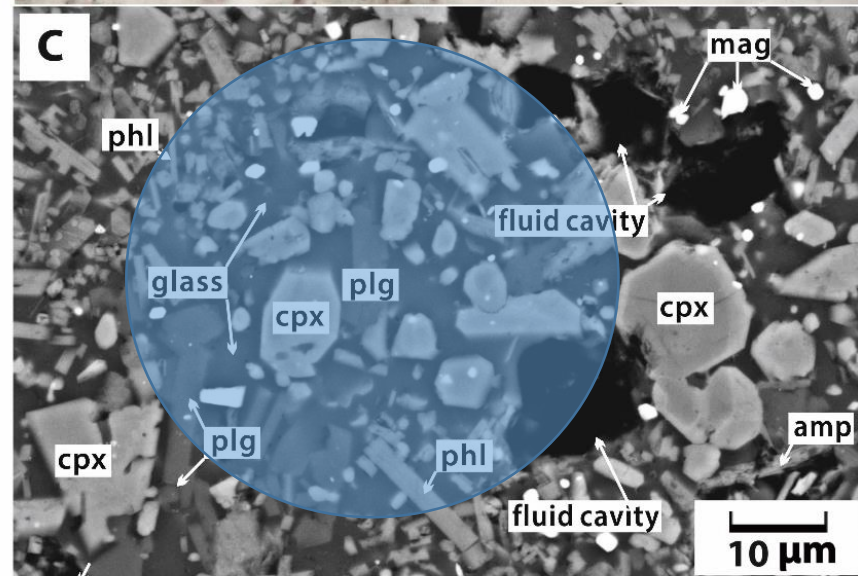
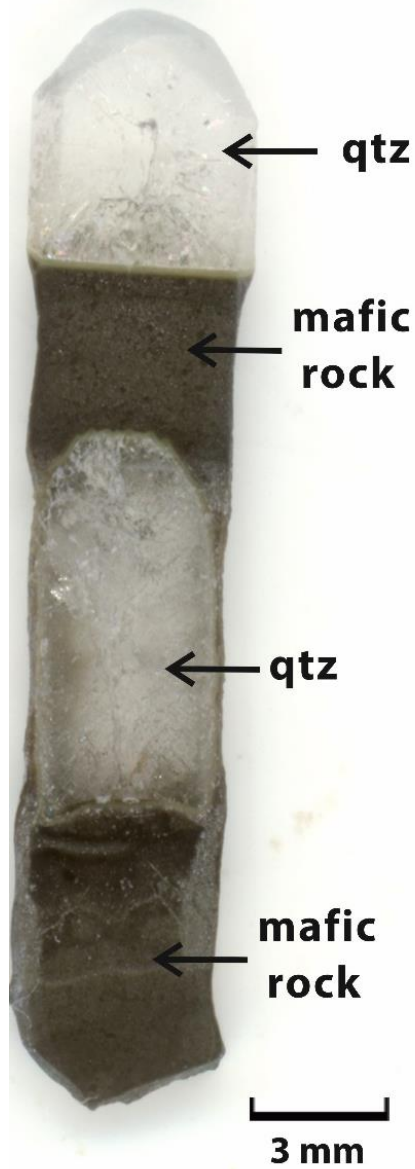
Borchert et al., 2010 Chem. Geol.

两种方式在低压 (<1GPa) 情况下结果类似

合成流体包裹体方法

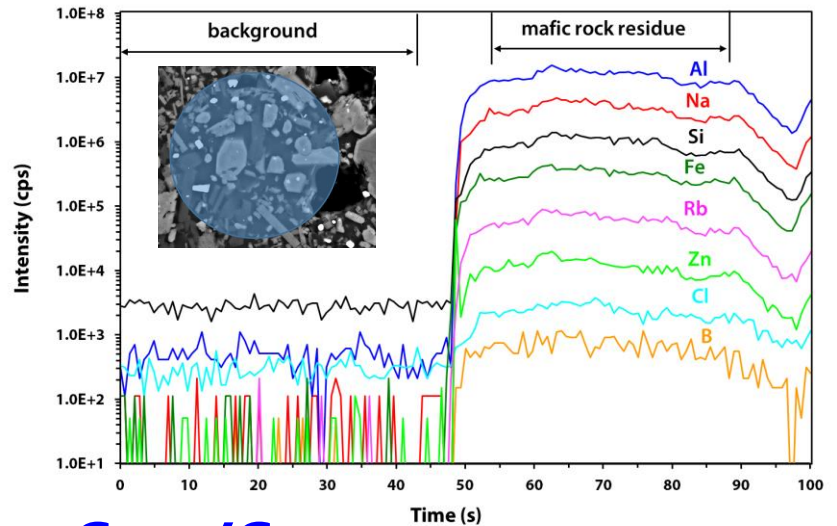
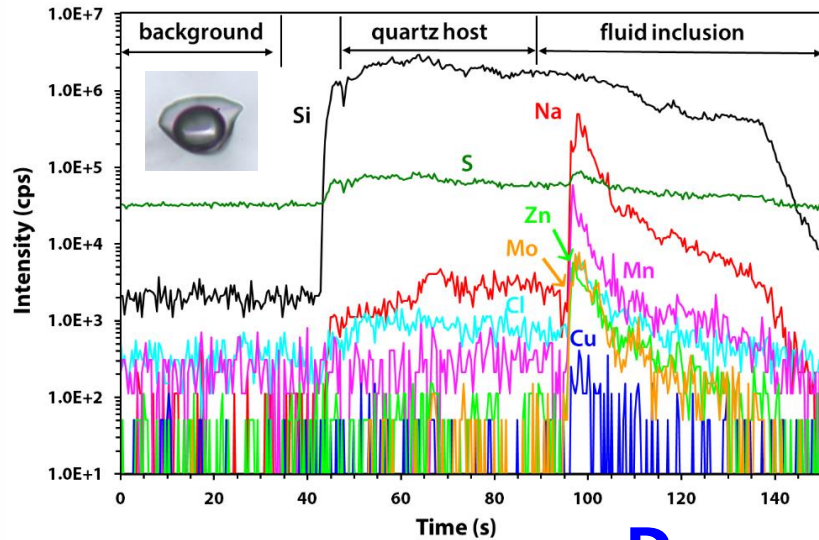


**850 °C, 2 kbar
> 7days**

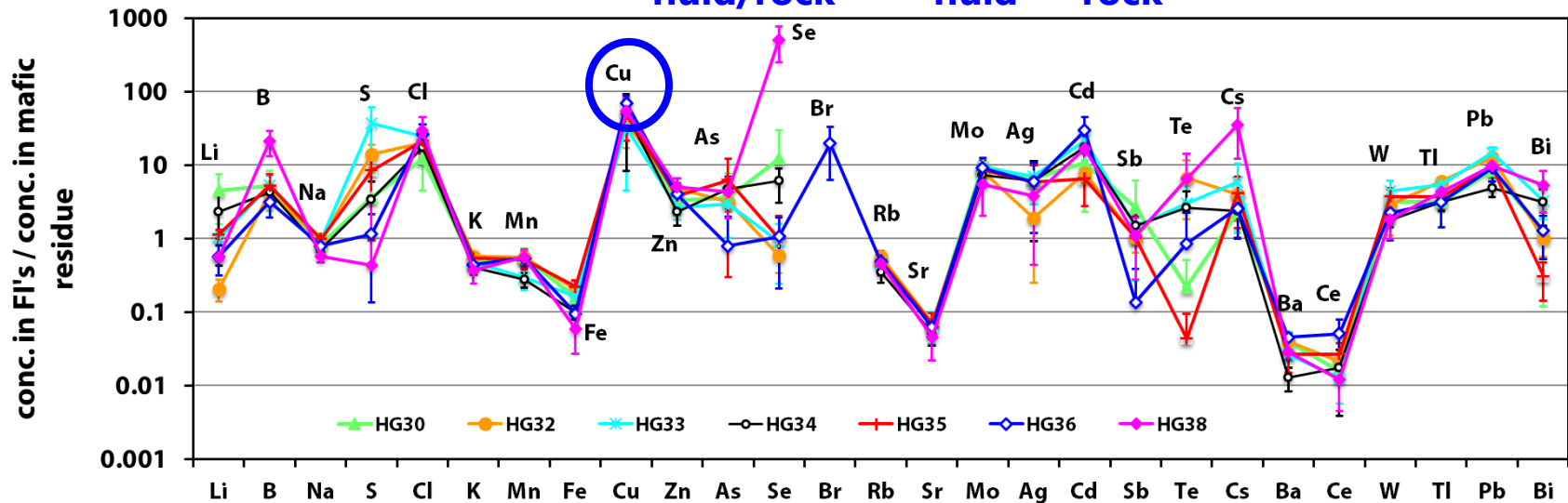


Guo & Audétat, 2017 GCA

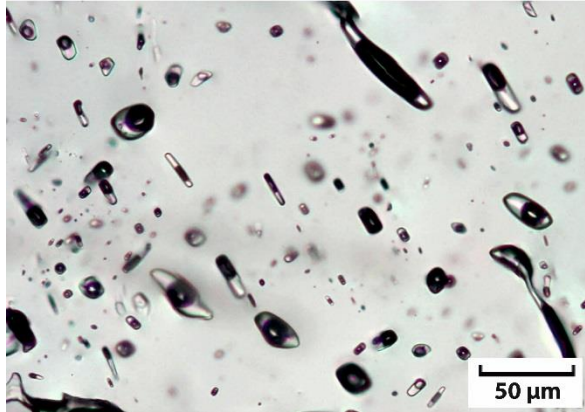
流体和岩石分配系数($D_{\text{fluid/rock}}$)



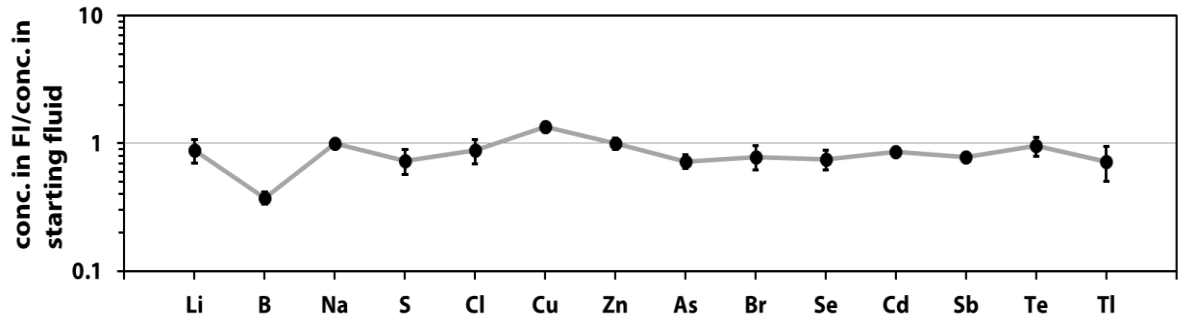
$$D_{\text{fluid/rock}} = C_{\text{fluid}} / C_{\text{rock}}$$



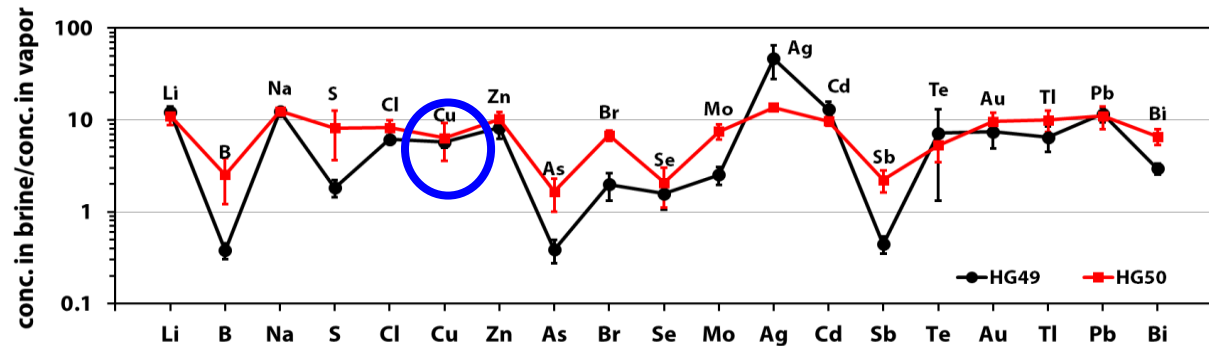
Brine/vapor 元素分配



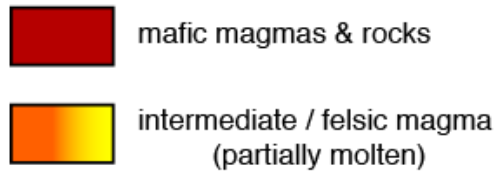
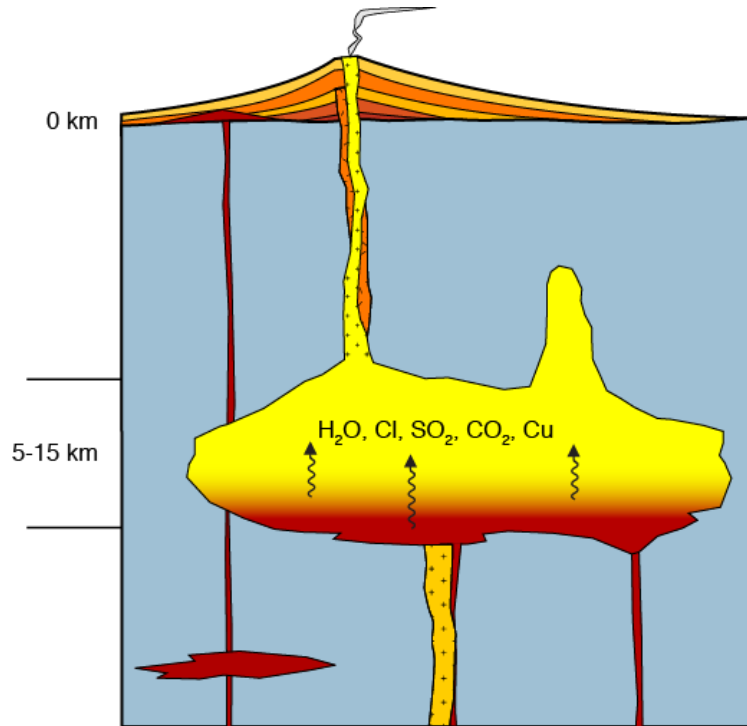
Single phase -800 °C, 2.3 kbar



Two phases- 800 °C, 1.3 kbar

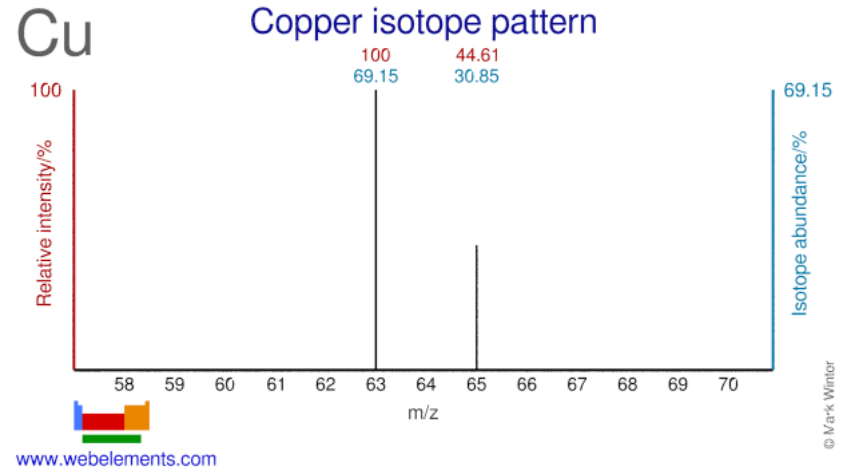


铜同位素在流体出溶过程分馏



Audétat and Simon (2013)

Cu

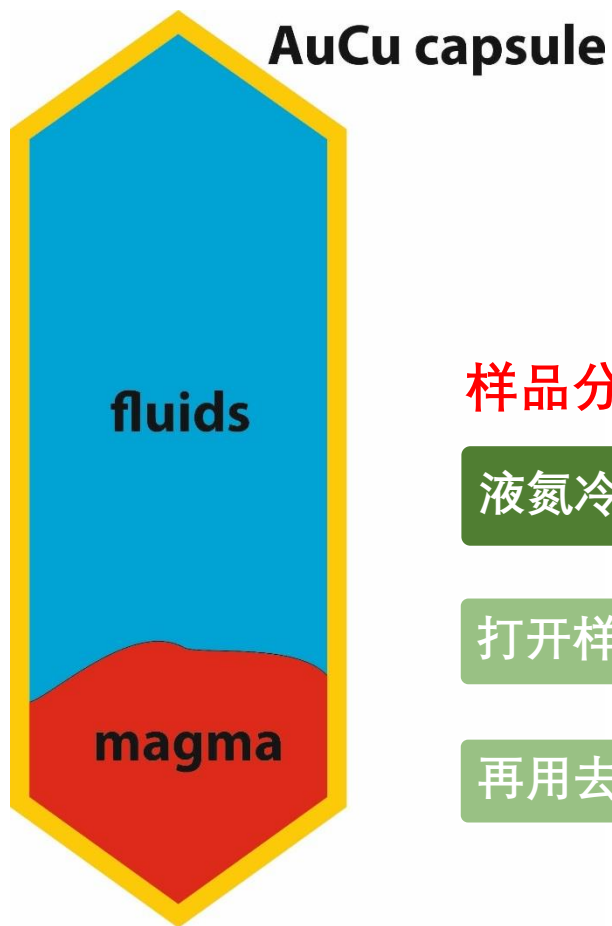


□ 流体活动性元素

□ 成矿元素

□ 铜同位素研究广泛

实验设计



实验条件

800-850 °C, 2 kbar 冷封式高压釜

起始材料

- 基性到酸性(安山岩、英安岩、流纹岩、淡色花岗岩)
- 0.5 -4 N HCl 溶液

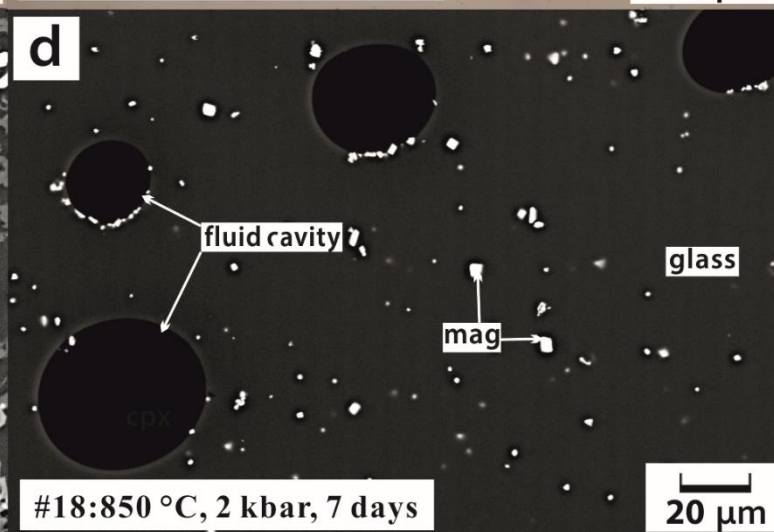
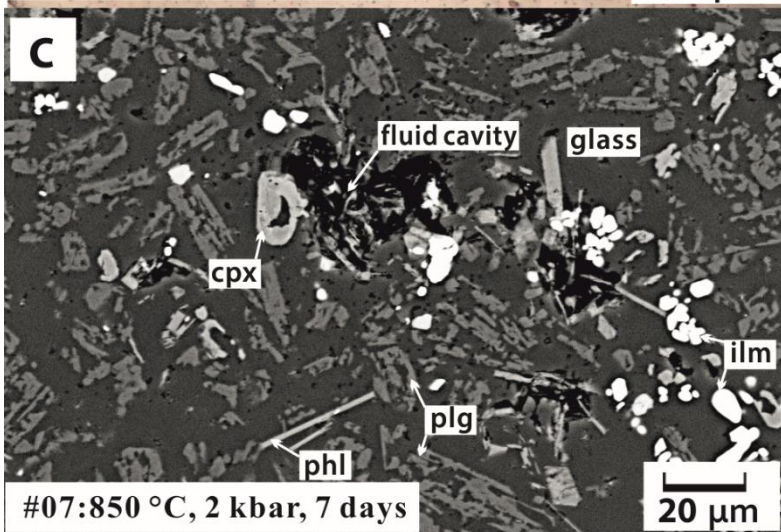
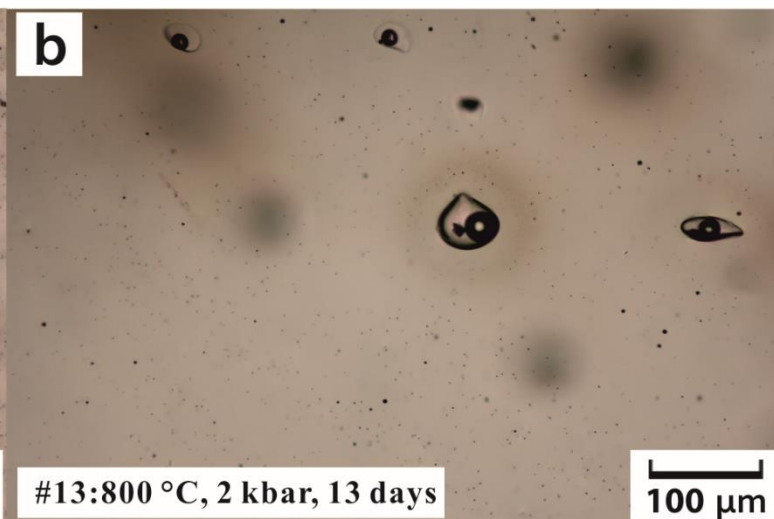
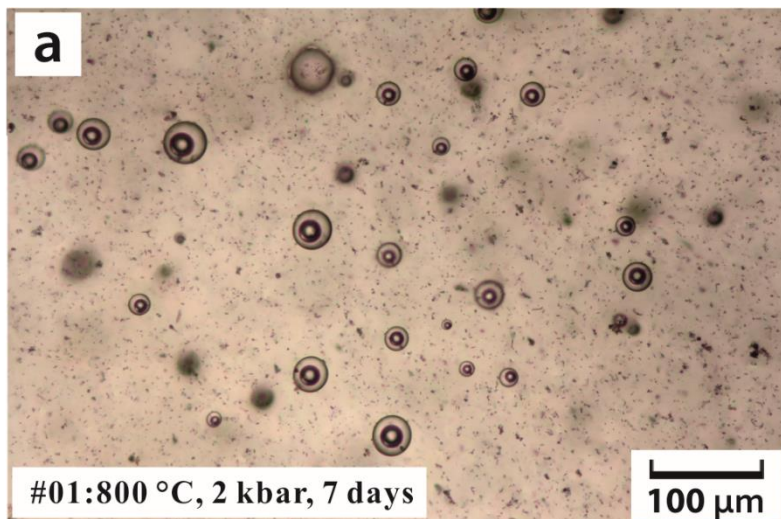
样品分离方案

液氮冷冻样品管

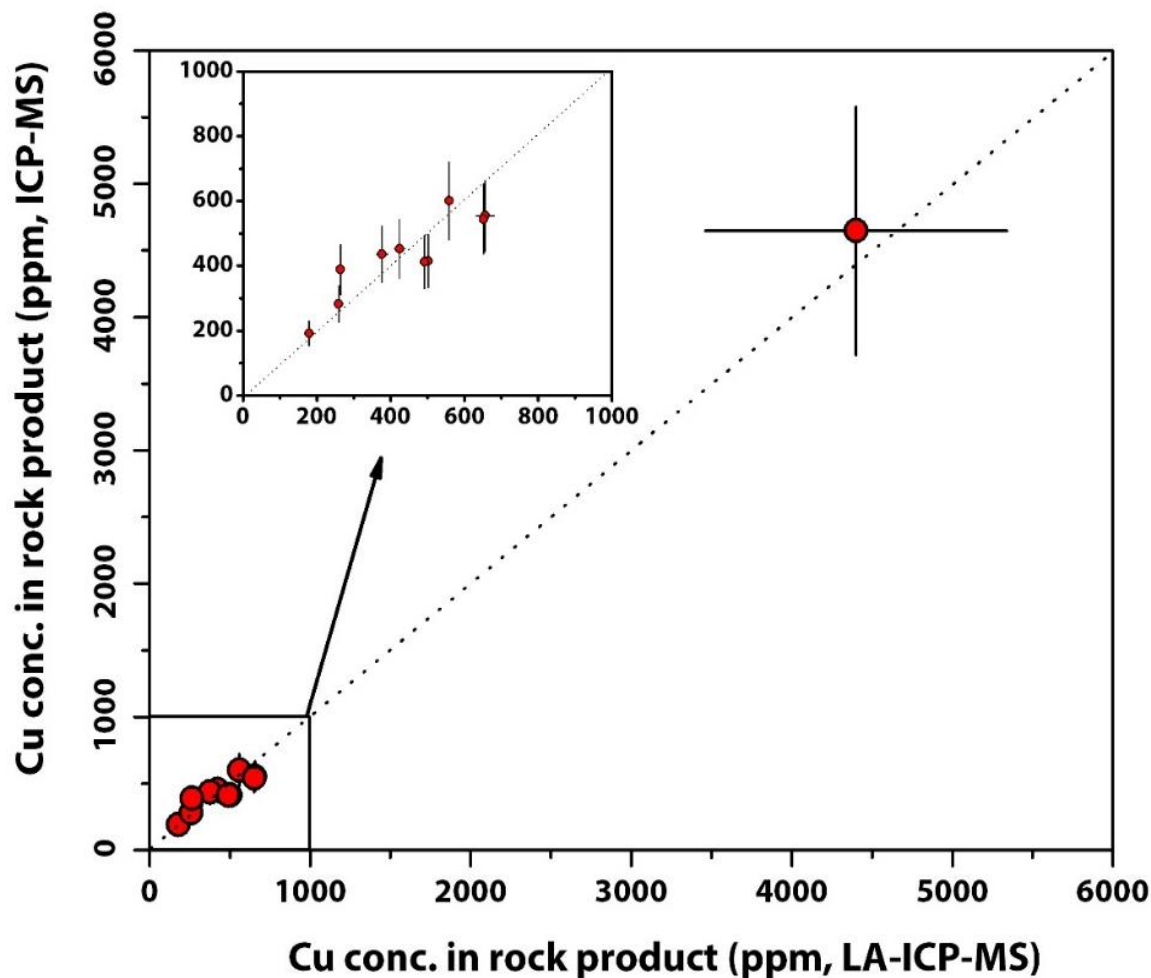
打开样品管，去离子水煮沸30分钟

再用去离子水清洗数次

实验样品



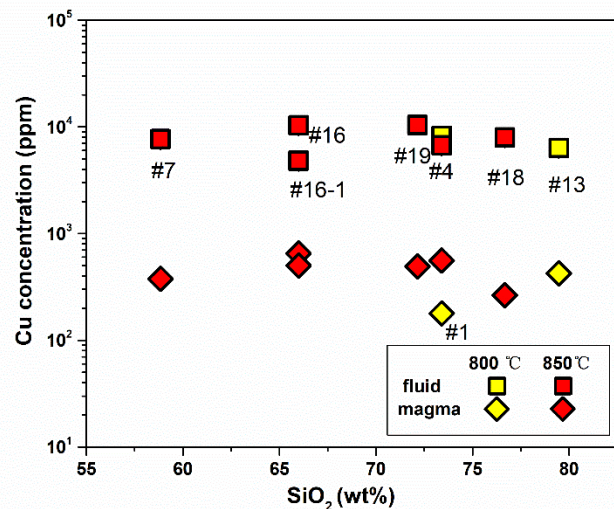
固体样品的原位和全分析对比



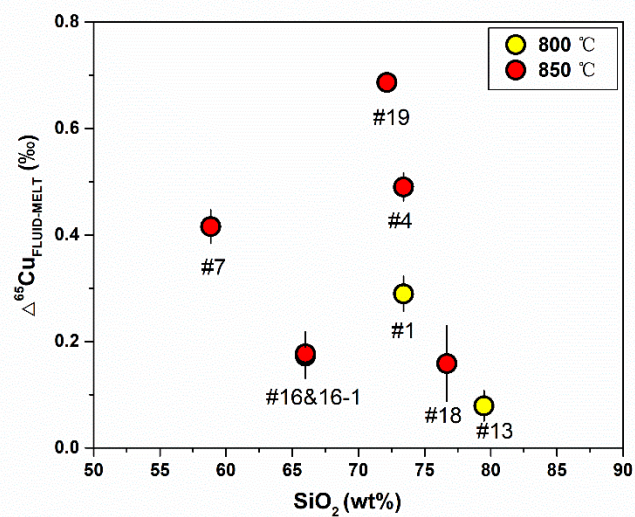
样品分离成功!!!

实验结果

a

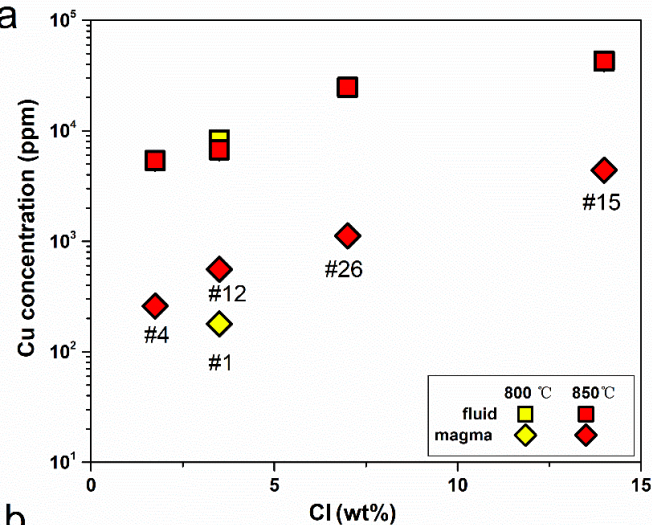


b

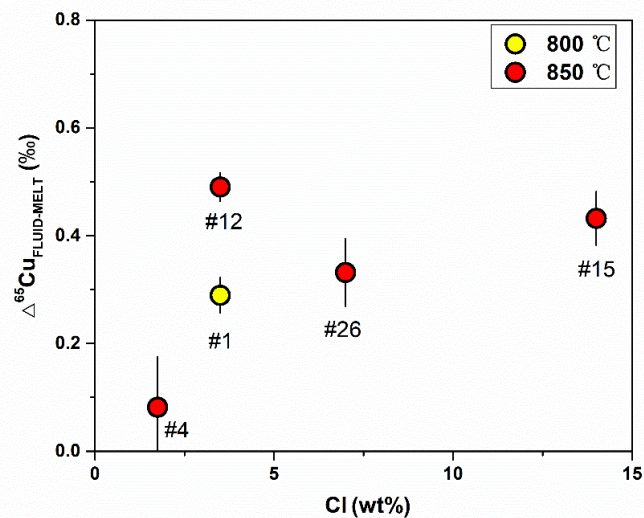


$\delta^{65}\text{Cu}$: 流体 > 岩浆

a



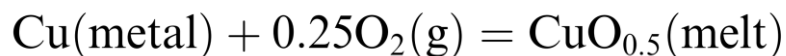
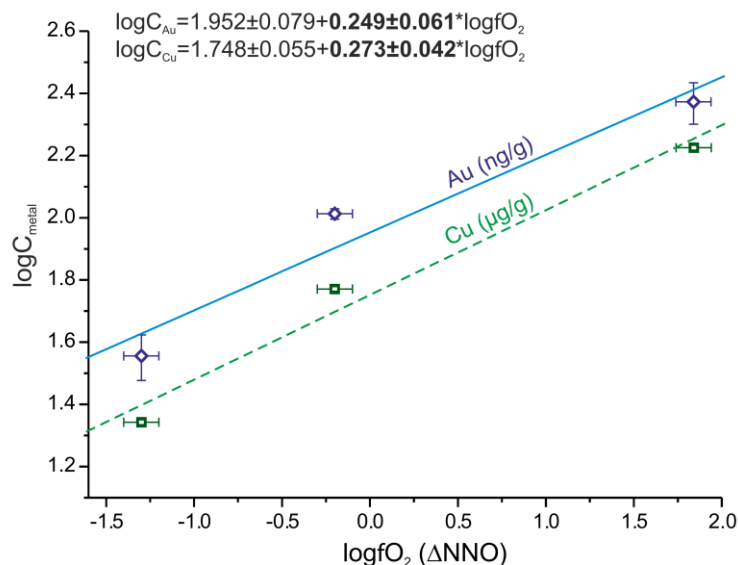
b



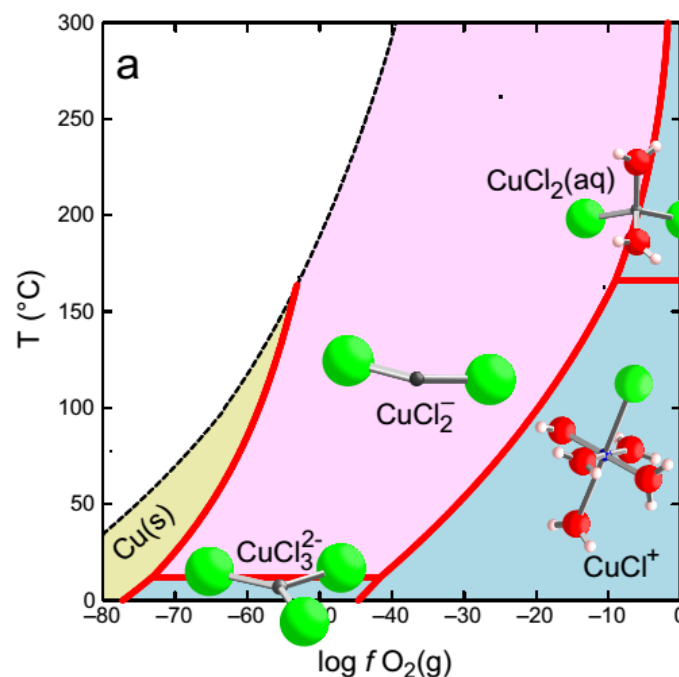
铜同位素分馏的可能机制

硅酸盐 : $\text{CuO}_{1/2}$ (Zajacz et al., 2012, 2013 GCA; Liu et al., 2014, 2015 GCA)

流体: $\text{CuCl}(\text{H}_2\text{O})$, CuCl_2^- , CuCl_3^{2-} (Sharman et al., 2013 GCA; Fujii et al., 2013, 2014 GCA)

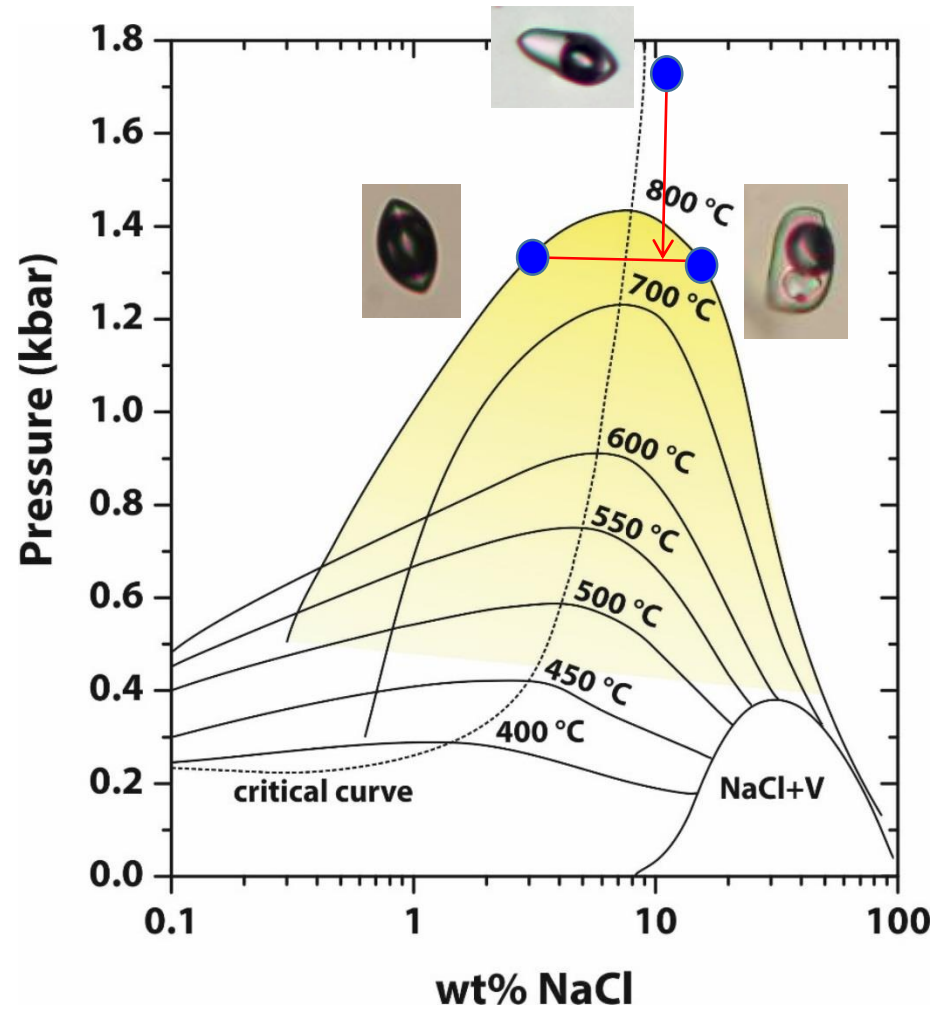


Zajacz et al., 2012 GCA

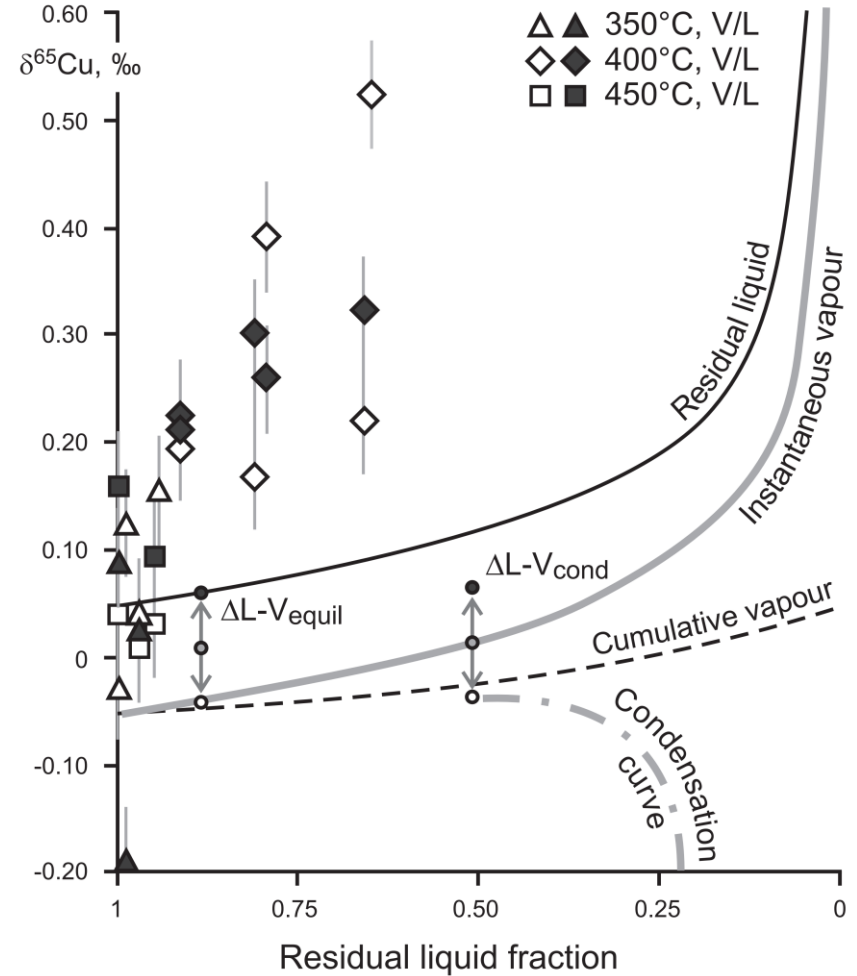


Brugger et al., 2016 Chem. Geol.

Brine/vapor 间Cu同位素分馏

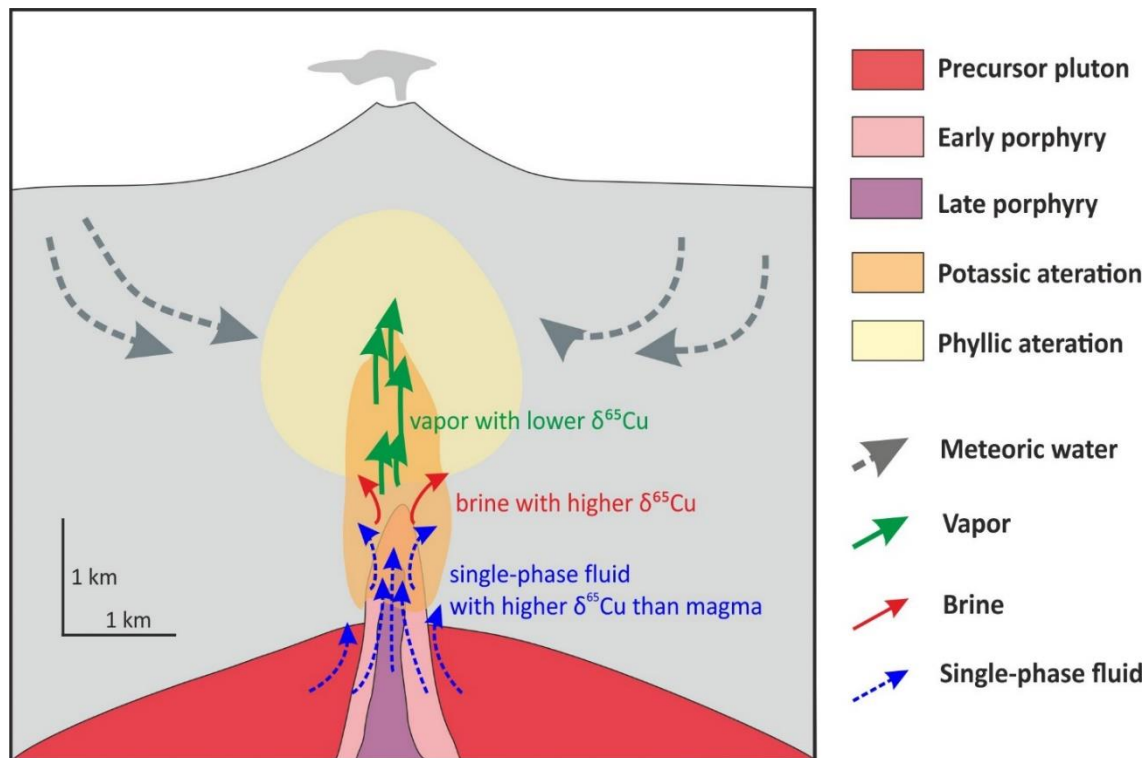


$\delta^{65}\text{Cu}$: brine > vapor

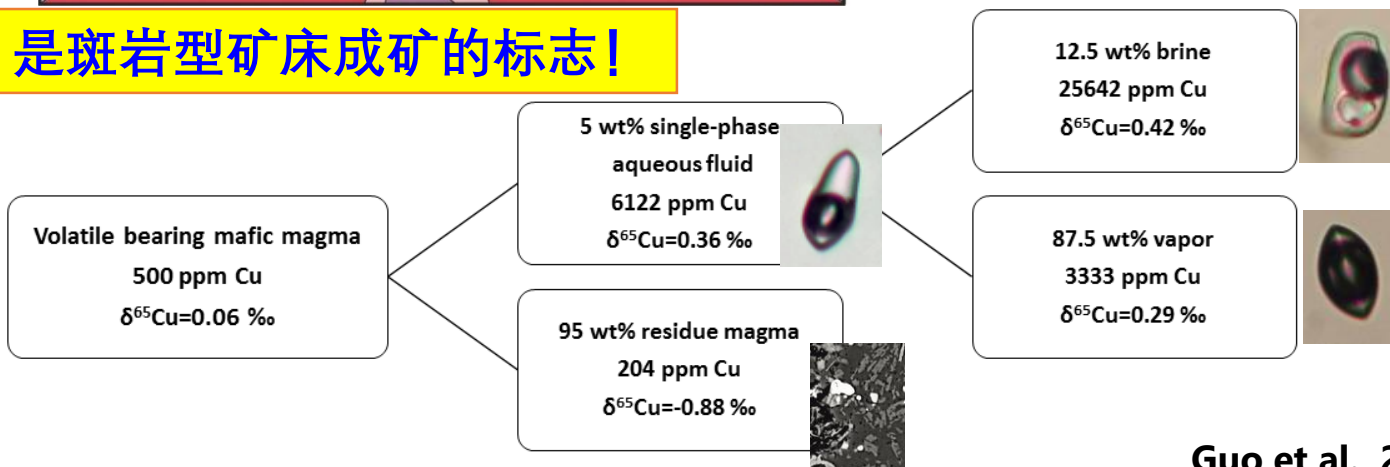


Rempel et al., 2012 GCA

示踪斑岩型铜矿的意义



高 $\delta^{65}\text{Cu}$ 是斑岩型矿床成矿的标志!



实验测定同位素平衡分馏系数

➤ 熔体-熔体 (金属, 硅酸盐, 硫化物...)

-核幔分异, 岩浆演化熔体不混融

➤ 熔体-矿物

-岩浆结晶分异

➤ 矿物-矿物

-变质过程, 地幔矿物平衡

➤ 熔体-流体

-流体出溶

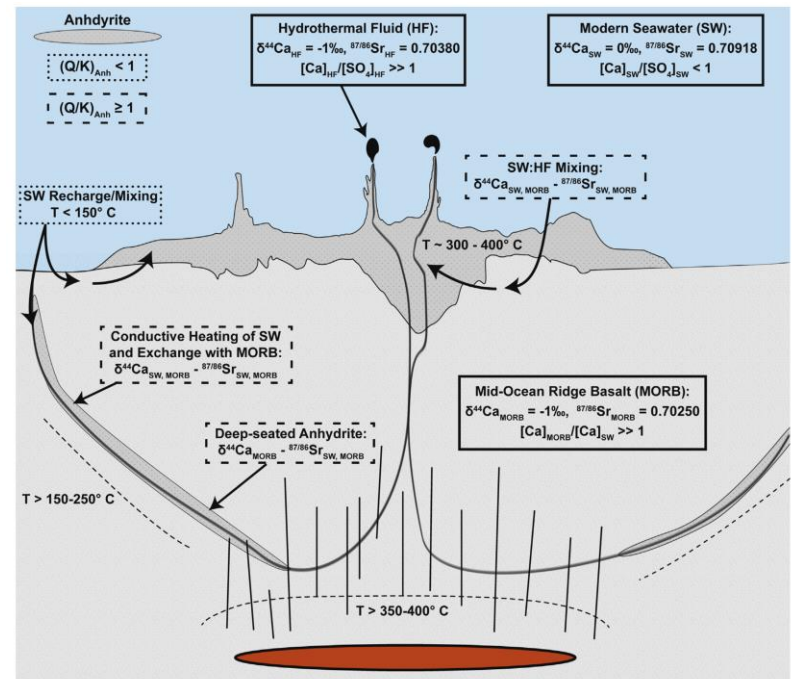
➤ 流体-矿物

-流体中矿物沉淀, 结晶

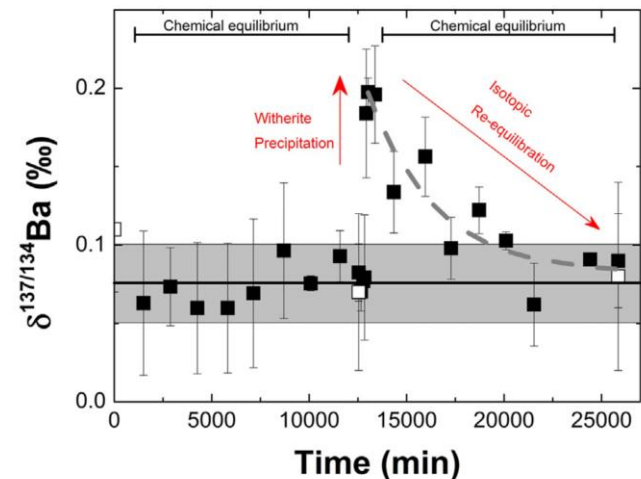
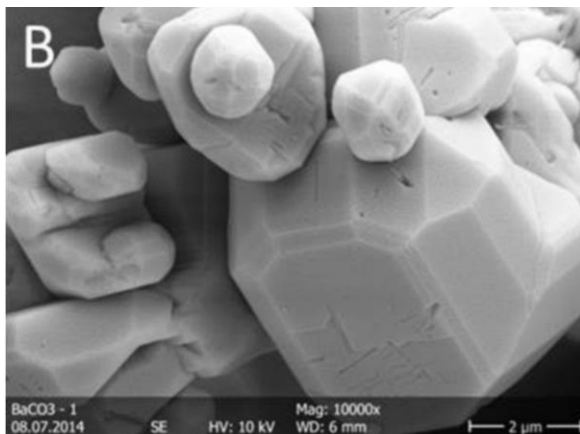
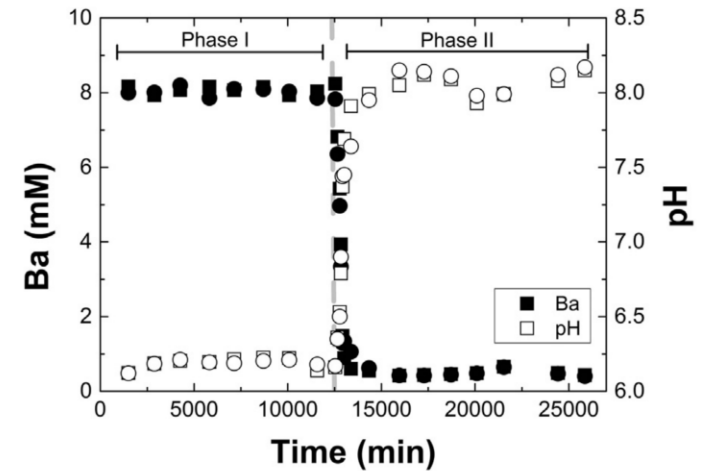
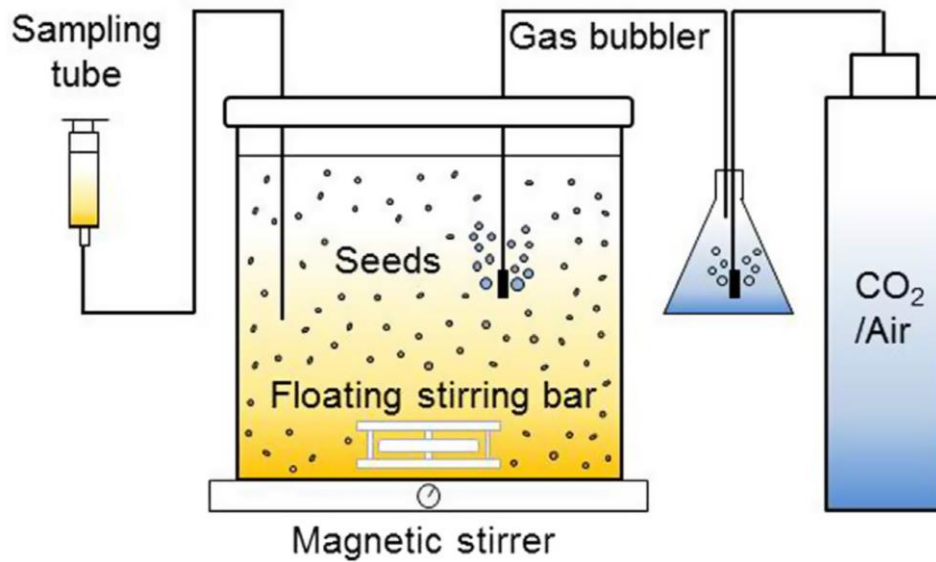
➤ 流体-流体 (流体不混融)

-流体沸腾, 液态不混溶

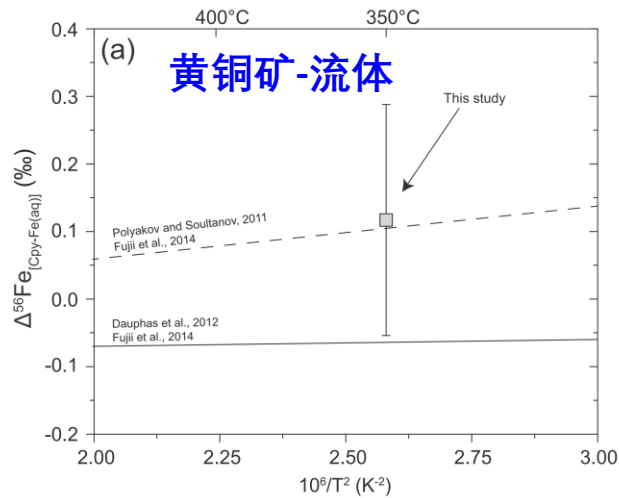
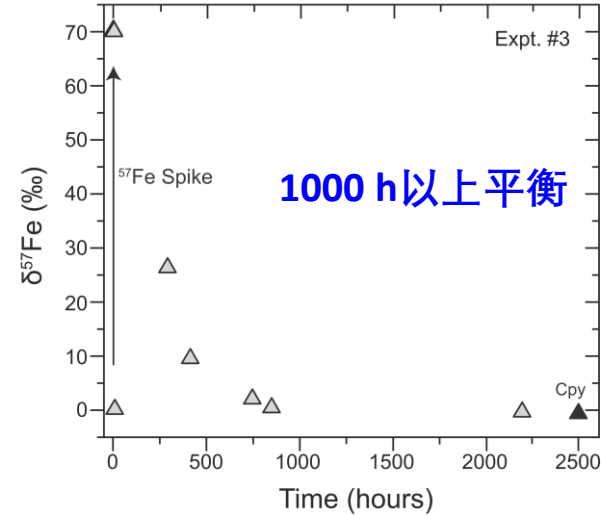
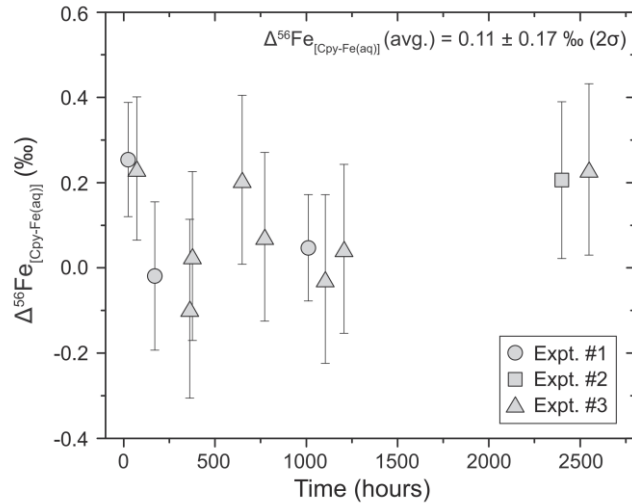
两相分离!



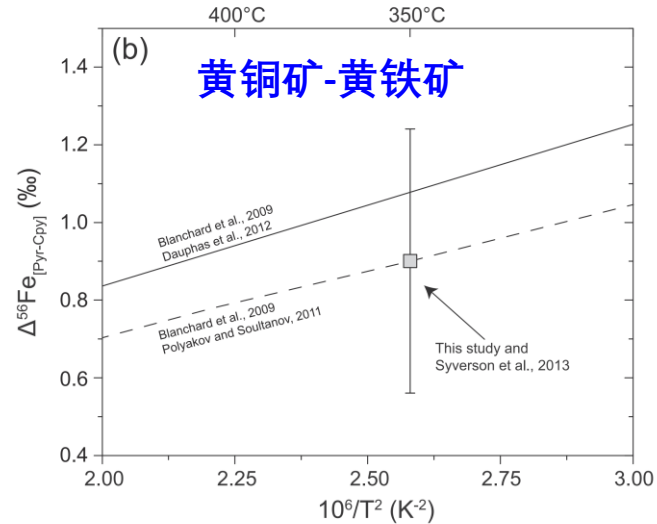
流体和毒重石 (BaCO_3) 之间Ba同位素平衡分馏



流体和黄铜矿之间Fe同位素平衡分馏



350 °C, 500 bar



Syverson et al., 2017 GCA

总结 和 展望

- 根据实际科学问题选取实验设备和实验方法
- 实验平衡，样品分离，测试精度
- 未来原位分析技术应用同位素分馏研究
- 实验设备的发展 $\leftrightarrow$ 分析技术改进



Thank you for attention!

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BGI: Andreas Audétat, Hans Keppler, Catherine McCammon, Ulrike Trenz, Raphael Njul , Detlef Krauß, Anke Potzel....

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McGill: Vincent van Hinsberg, Don Baker

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