2005年全国岩石学与地球动力学会前专题讲座-同位素地质年代学与地球化学

Re-Os地质年代学与地球化学

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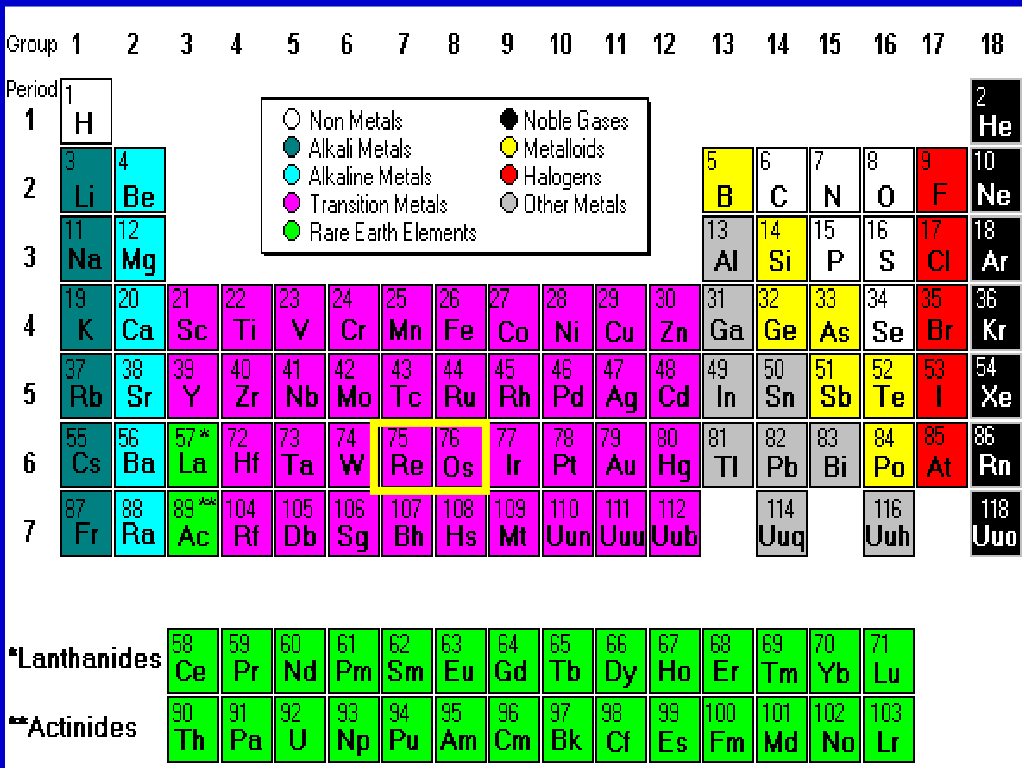
讲座提纲

- Re-Os同位素体系基本特征
- 化学分离与质谱测定
- Re-Os同位素年代学
- Re-Os同位素地球化学

1. Re-Os同位素体系基本特征



Lu-Hf 同位素组称

Re:
^{185}Re (37.07%)
^{187}Re (62.93%)

Os:
^{184}Os (0.018%)
^{186}Os (1.59%)
^{187}Os (1.64%)
^{188}Os (18.3%)
^{189}Os (16.1%)
^{190}Os (26.4%)
192Os (41.0%)

$$^{187}\text{Re} \xrightarrow{\beta\text{ - decay}} {}^{187}\text{Os}$$

$T_{1/2} = 5\times10^{9}$ year、 $\lambda_{187Re} = 1.666\times10^{-11}/y$

常见岩石的Re、Os含量年（Shirey and Walker, 1998）

	Re (ng/g)[a]	Os (ng/g)	$^{187}Re/^{188}Os$
Chondrites			
Allende[b]	63.23	773.9	0.3935
O,C,E[b]	42.3–96.96	417.9–1048	0.3731–0.4779[c]
Irons			
IIAB[d]	0.778–4,816	8.808–65,740	0.3526–0.9396
Mantle			
Fertile[b,e]	0.25–0.30	2.8–3.4	0.401
Depleted[f]	0.051–0.135	0.8–9	0.06–1
Komatiite[g]	0.5–1.5	0.5–6	1–6
MORB[g]	0.5–2	0.001–0.05	100–5,000
OIB[g]	0.1–1	0.01–0.5	20–3,000
Average continental crust[h]	<1	<0.05	~50
Pelagic sediment[i]	0.076–1.49		
Black shale[j]	517	2.46[k]	18,780
Minerals			
Chromite[l]	0.22–0.64	13–67	0.02–0.2
Molybdenite[m]	0.7–160 ppm	Radiogenic	Very high
Sulfide[n]			
E-type	52–357	4.7–122	5.2–104
P-type	300–2,551	6,000–10,000	0.24–2.0

Re-Os的地球化学性质

Re中等不相容元素，Os相容元素

Re和Os为高度亲硫元素

Re和Os在硫化物中相对比较富集，在硅酸盐相中含量很低

Re和Os主要富集在地核中；Re在地壳中相对富集，Os在地幔中相对富集

Re-Os化学分离与质谱测定

1. 碱熔法 (Na_2O_2, NaOH)

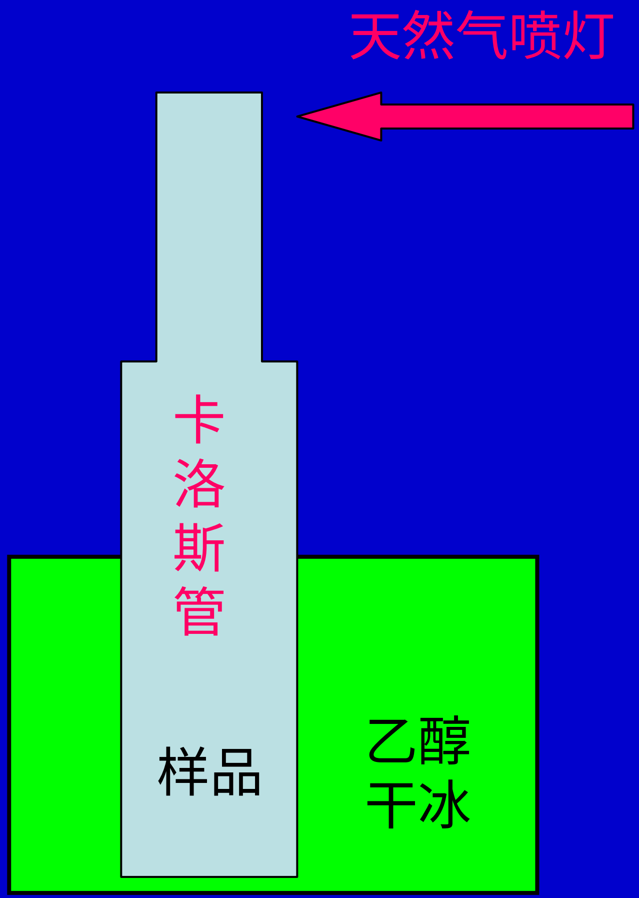
确保难熔矿物分解和样品与稀释剂同位素平衡；实验流程长，流程本底高

2. 酸溶法

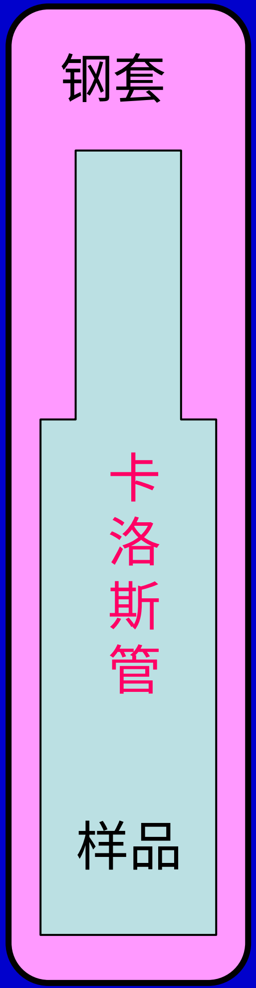
本底低，但不能确保样品和稀释剂同位素平衡，挥发性OsO4易逸出，实验重复性差

3. 卡洛斯管高温高压熔样（王水或反王水）

本底低，完全溶解样品，确保样品和稀释剂同位素平衡，溶样时保持密闭，装样和取样时保持低温环境，可防止挥发性OsO4逸出



卡洛斯管装样
和取样示意图

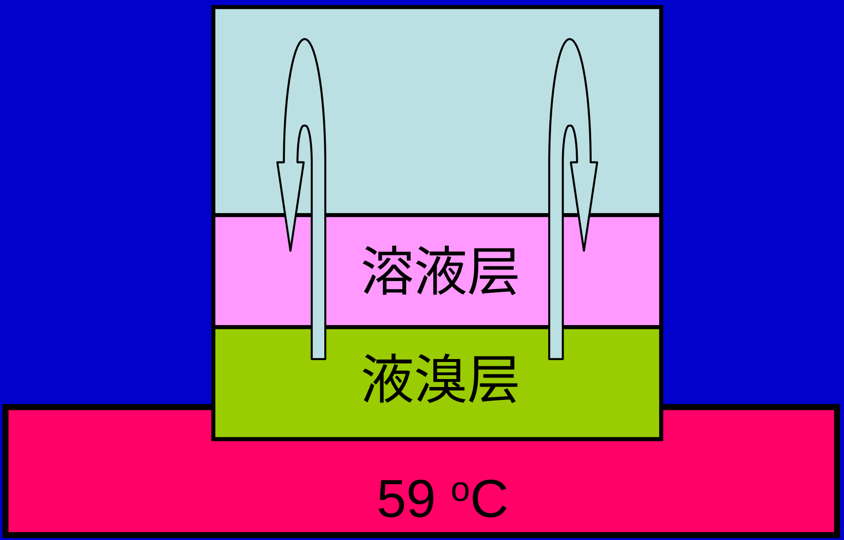


卡洛斯管高温
高压溶样

Os分离纯化

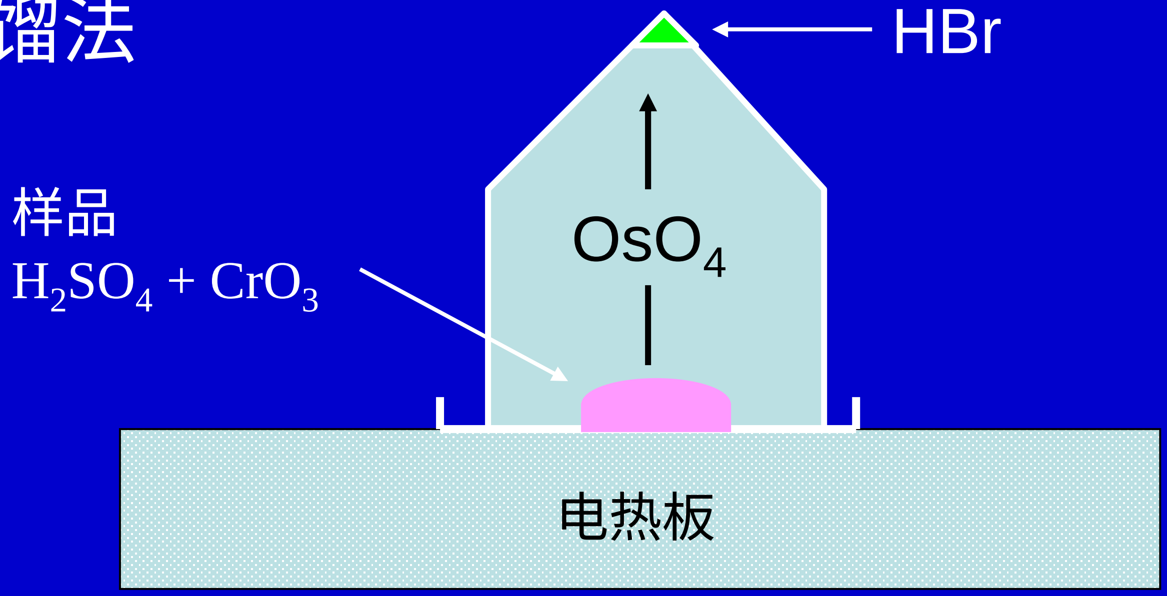
1. 溴提取法

$$OsO_4 + HBr \longrightarrow OsBr_6^{2-}$$



Os分离纯化

2. 微蒸馏法



Re分离纯化

—离子交换树脂分离纯化

质谱测定-负离子发生器

3. Re-Os 同位素地质年代学

Geochronological applications of Re-Os are limited due to the very low concentrations of Os in most minerals and rocks.

Re-Os geochronology has applied on dating the formation of iron meteorites, platinum group metal ores, and some ultramafic rocks.

Re is strongly concentrated in molybdenite (MoS_2) and some copper-sulfides. Hence, the Re-Os system can be suitable for dating certain types of sulfide ore deposits.

Re-Os同位素定年的基本原理

$$^{187}Re \longrightarrow {}^{187}Os$$

$$(^{187}Os/^{188}Os)_t = (^{187}Os/^{188}Os)_i + {}^{187}Re/^{188}Os(e^{\lambda t}-1)$$

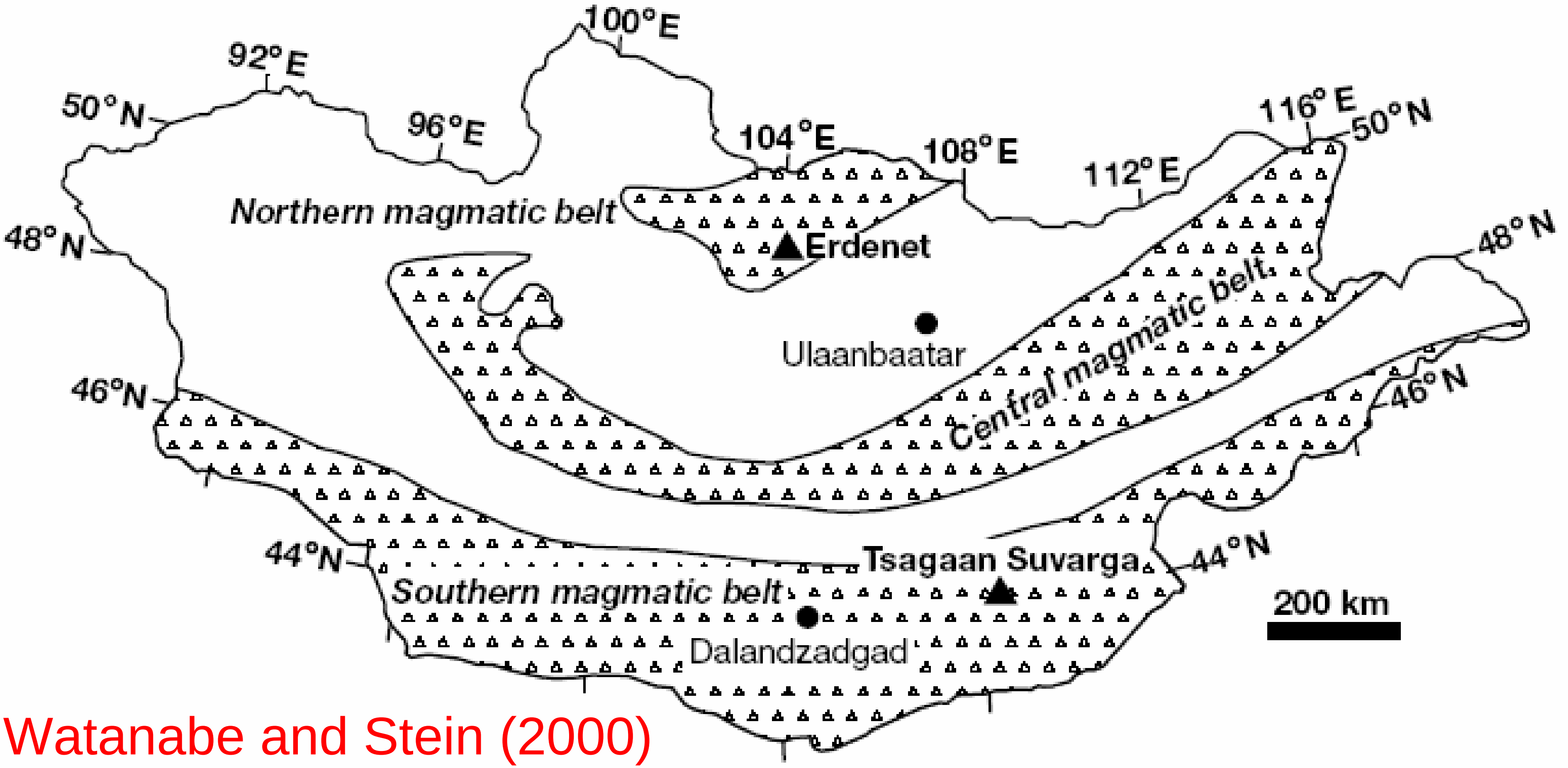
和其它等时线一样，Re-Os等时线也必须满足等时、同源和封闭等条件。

（1）辉钼矿Re-Os定年

$$({}^{187}Os/{}^{188}Os)_t = ({}^{187}Os/{}^{188}Os)_i + {}^{187}Re/{}^{188}Os(e^{\lambda t}-1)$$

对于辉钼矿，由于其Re、Os含量较高，其初始Os可以忽略不计，因而此时既可对单个样品进行定年，也可运用等时线方法定年。

$$^{187}Os = {}^{187}Re(e^{\lambda t}-1)$$



Watanabe and Stein (2000)

TABLE 1. Re-Os Ages for Molybdenite from Erdenet and Tsagaan Suvarga Cu-Mo Deposits, Mongolia

Deposit	AIRIE Run	Re (ppm) [1]	^{187}Re (ppm) [1]	^{187}Os (ppb) [1]	Age (Ma) [2, 3, 4]
Erdenet (ER)	CT-28	538.6 (5)	338.5 (3)	1360 (2)	240.7 ± 0.8
	CT-50	530.6 (8)	333.5 (5)	1338 (2)	240.4 ± 0.8
					240.6 ± 0.6
Tsagaan Suvarga (TS)	CT-29	80.03 (6)	50.30 (3)	311.1 (3)	370.1 ± 1.2
	CT-51	155.5 (1)	97.76 (9)	605.5 (6)	370.6 ± 1.2
					370.4 ± 0.8

Sun et al (2003).

Ecno. Geol., 98: 175-180.

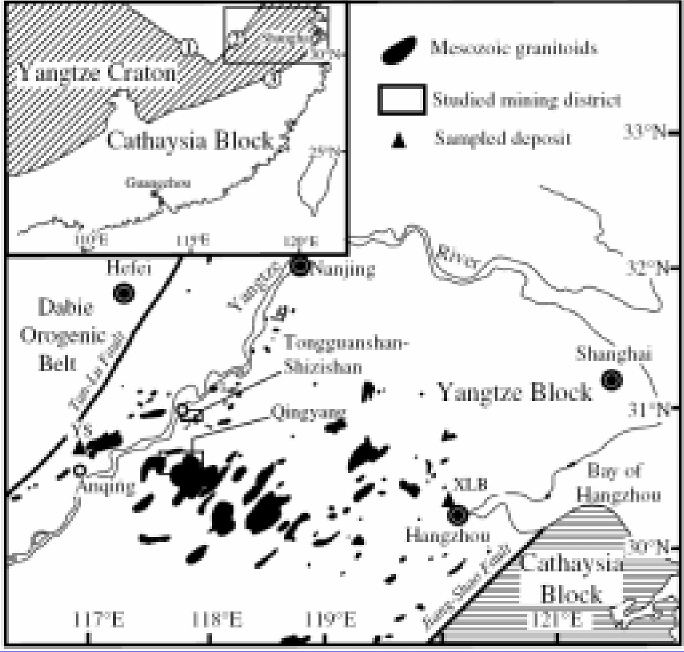


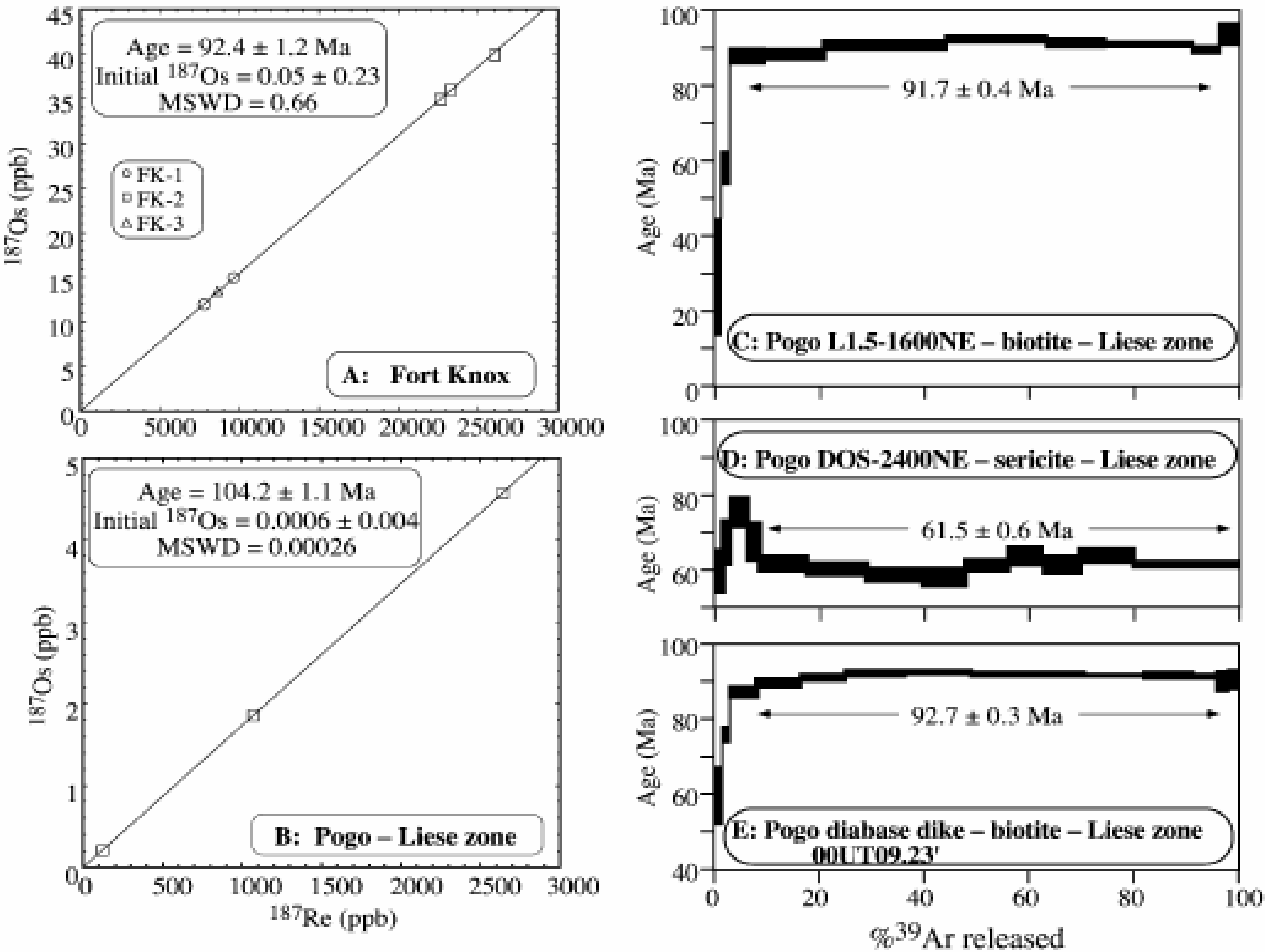
TABLE 1. Os Isotope Ratios after Irradiation and Os-Os Ages of Molybdenites from the Cu and Mo Deposits of the Middle and Lower Yangtze Region

Sample no.	Location	$^{186}Os/^{187}Os$[1]	$^{188}Os/^{187}Os$[1]	t_{186} (Ma)	t_{188} (Ma)	T_{avg} (Ma)
HLP (standard)	Huanglongpu	0.001979 ± 4	0.001684±5	221.5	221.5	
YS-4	Yueshan	0.00316±2	0.00280±2	138.8±1.3	133.3±1.5	136.1±2.0
TL-7	Longhushan	0.00315±2	0.00273±3	139.3±1.4	136.7±2.1	138.0±2.5
TL-2	Shanxingshan	0.00323±2	0.00266±3	135.8±1.3	140.3±2.2	138.1±2.5
TL-4	Shenglilinchang	0.00320±2	0.00275±3	137.1±1.3	135.7±2.1	136.4±2.5
XLB-1	Xianlinbu	0.00333±1	0.00277±1	131.7±0.8	134.8±1.1	133.2±1.4
XLB-1	Duplicate	0.00333±1	0.00277±1	131.7±0.8	134.8±1.1	133.2±1.4

[1] Error in 6th decimal place for the HLP and 5th decimal place for other samples

TABLE 2. A Comparison of the Os-Os and Re-Os Dates of Molybdenites from the Cu and Mo Deposits in the Middle and Lower Yangtze Region

Sample no.	Location	Re (ppm)	^{187}Os (ppb)	Re-Os date (Ma)	Os-Os date (Ma)
TL-7	Longhushan	12.68±0.03	18.48±0.01	139.02±0.34	138.0±2.5
XLB-1	Xianlinbu	20.30±0.07	28.10±0.02	132.05±0.47	133.2±1.4
XLB-1	Duplicate		27.86±0.01	130.92±0.45	133.2±1.4


Age = 92.4 ± 1.2 Ma
Initial 187Os = 0.05 ± 0.23
MSWD = 0.66
FK-1
FK-2
FK-3
A: Fort Knox
187Os (ppb)
Age = 104.2 ± 1.1 Ma
Initial 187Os = 0.0006 ± 0.004
MSWD = 0.00026
B: Pogo – Liese zone
187Re (ppb)
91.7 ± 0.4 Ma
C: Pogo L1.5-1600NE – biotite – Liese zone
D: Pogo DOS-2400NE – sericite – Liese zone
61.5 ± 0.6 Ma
92.7 ± 0.3 Ma
E: Pogo diabase dike – biotite – Liese zone
00UT09.23'
Age (Ma)
%39Ar released

(2) 铁陨石定年

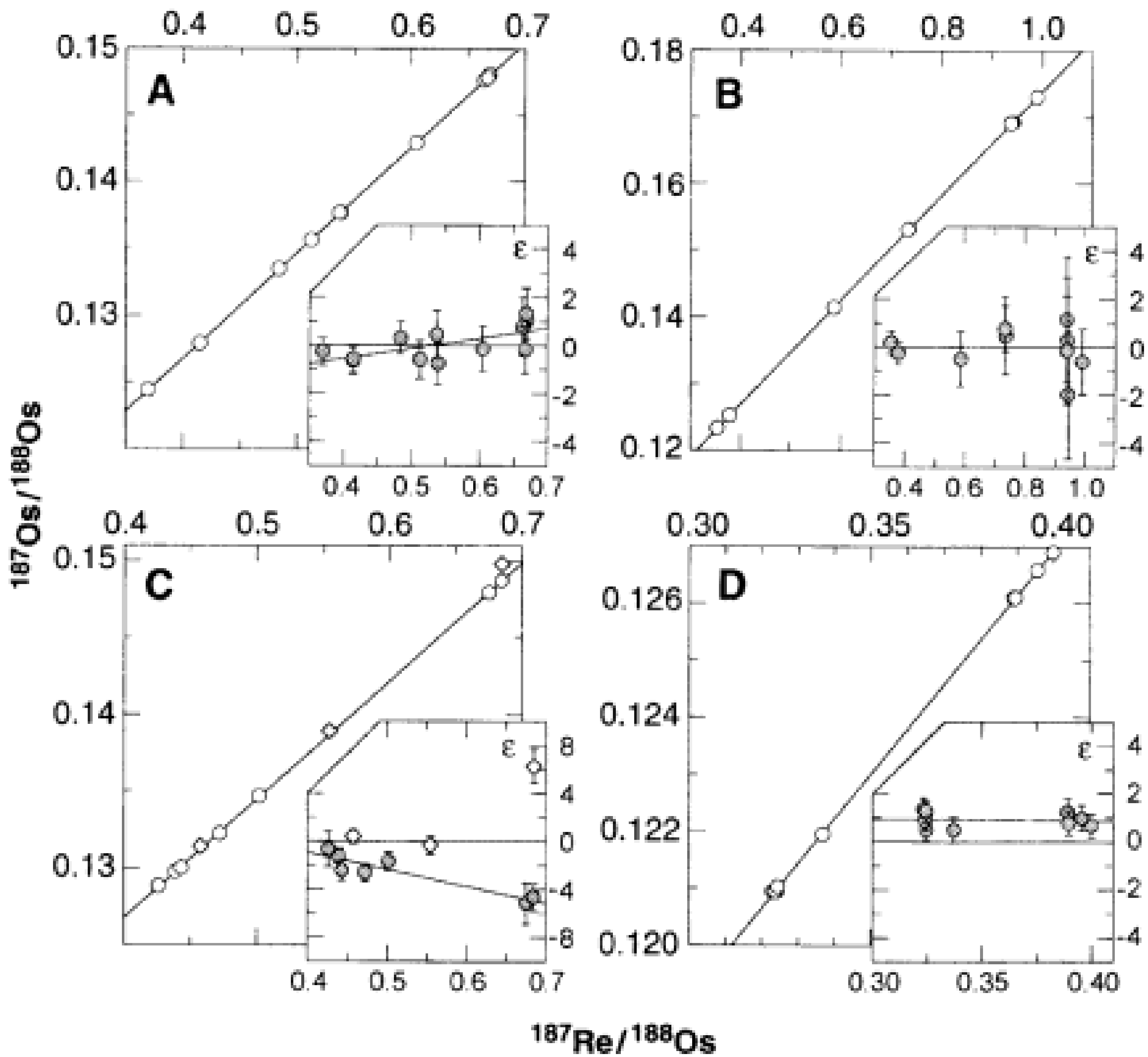
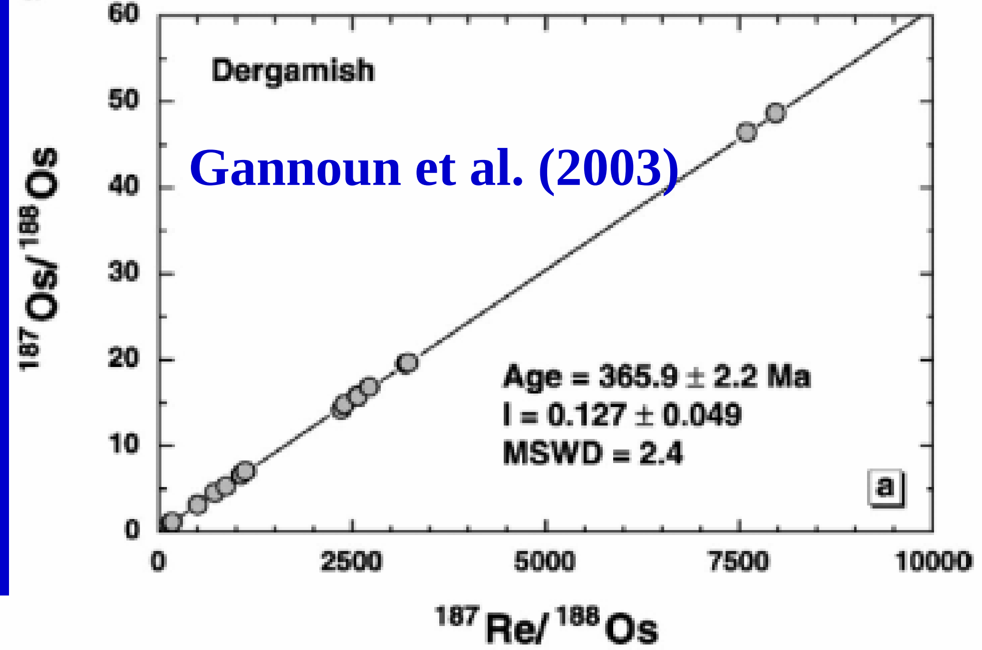


Fig. 1. Re-Os isochrons for (**A**) IIIA, (**B**) IIA, (**C**) IVA, and (**D**) IVB iron meteorites. The insets show the deviation in parts per 10,000 of data points from the best fit line in ε units: $\varepsilon = [(^{187}Os/^{188}Os) - S(^{187}Re/^{188}Os - I_O)] \times 10^4$, where S and I_O denote the isochron parameters of slope and initial $^{187}Os/^{188}Os$ ratio, respectively. For all meteorites, ε was calculated relative to the IIA isochron (represented by horizontal lines on the insets). Error bars on the insets account for uncertainties in both $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ ratios. The three IVA irons that were omitted in the isochron regression are shown as open diamonds.

Group	I_O	Slope	Age (Ma)	MSWD
IIA	0.09544 ± 7	0.07851 ± 14	4537 ± 8	1.15
IIIA	0.09524 ± 11	0.07887 ± 22	4558 ± 12	1.47
IVA	0.09584 ± 23	0.07721 ± 46	4464 ± 26	1.57
IVB	0.09559 ± 19	0.07834 ± 52	4527 ± 29	1.44

(3) 硫化物定年



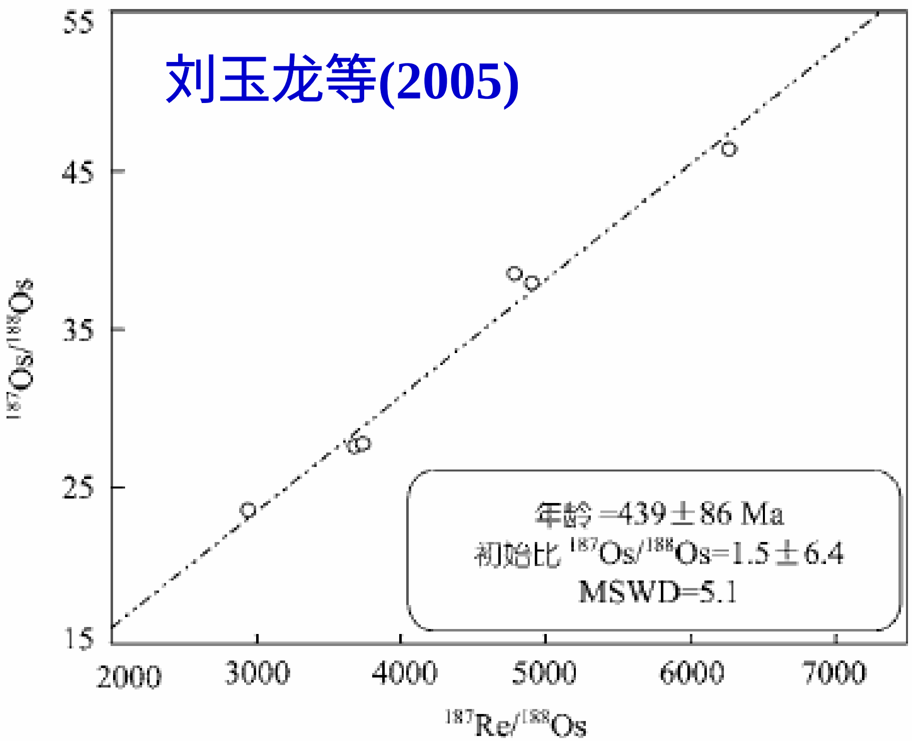
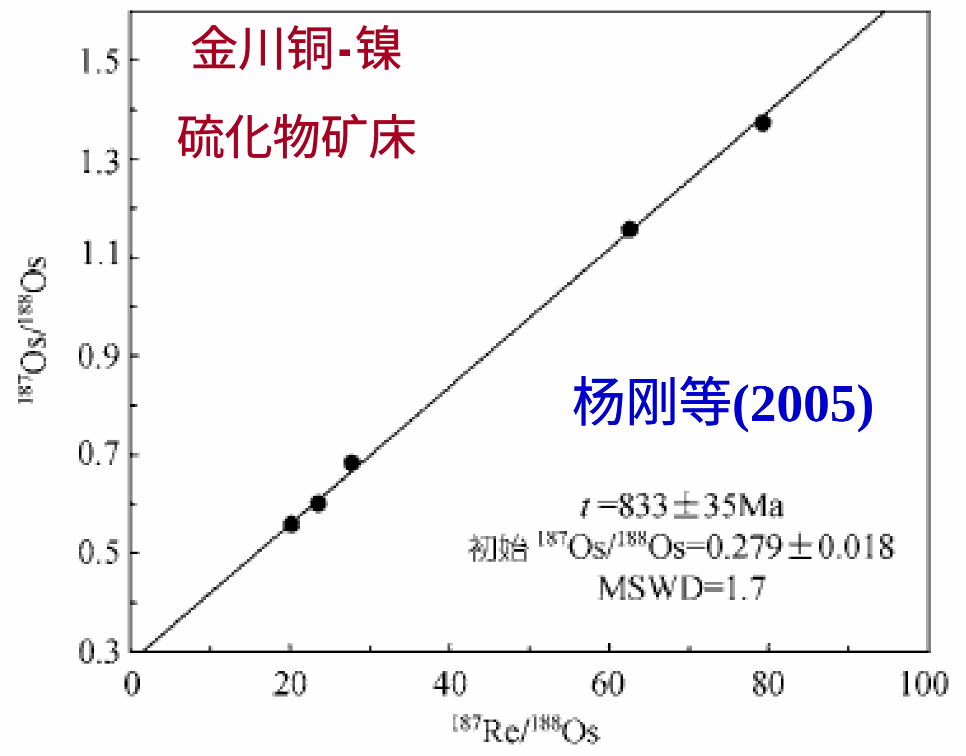
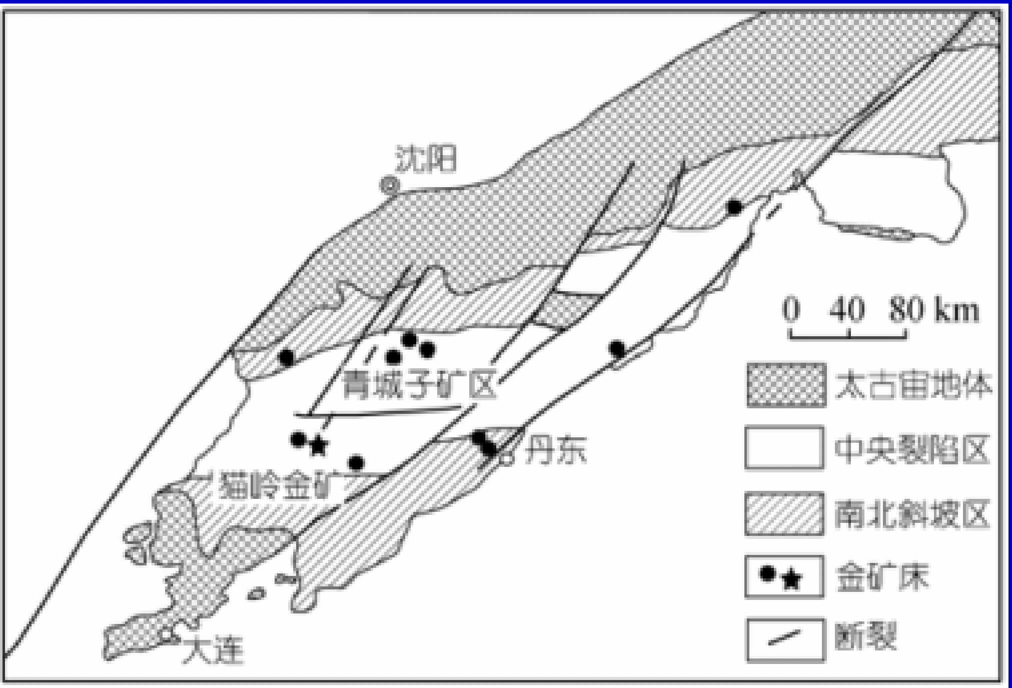


图 2 白云鄂博矿床黄铁矿 Re-Os 等时线年龄



辽东猫岭金矿硫化物定年（喻刚等, 2005）



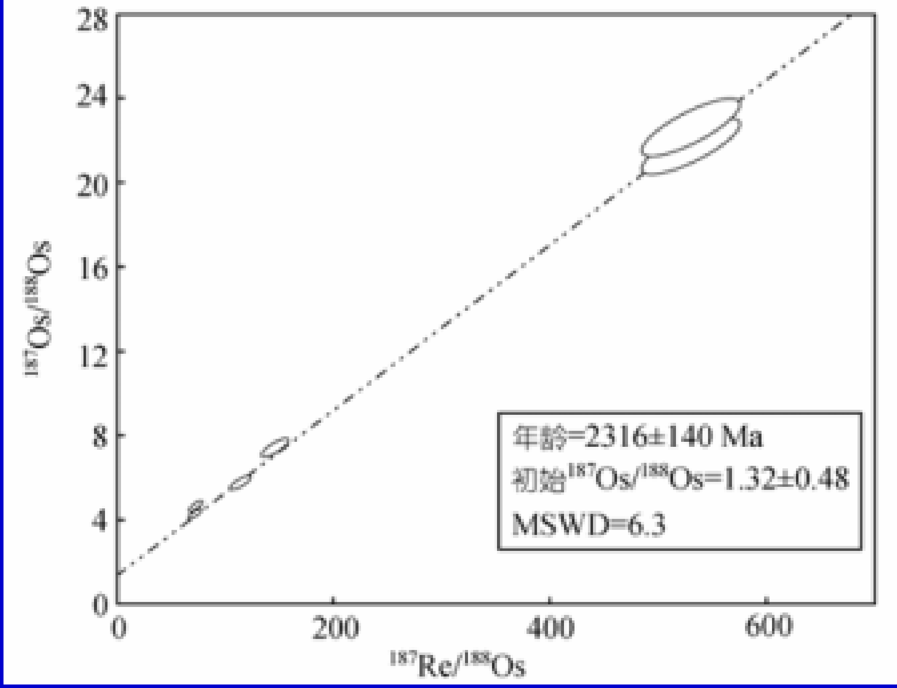


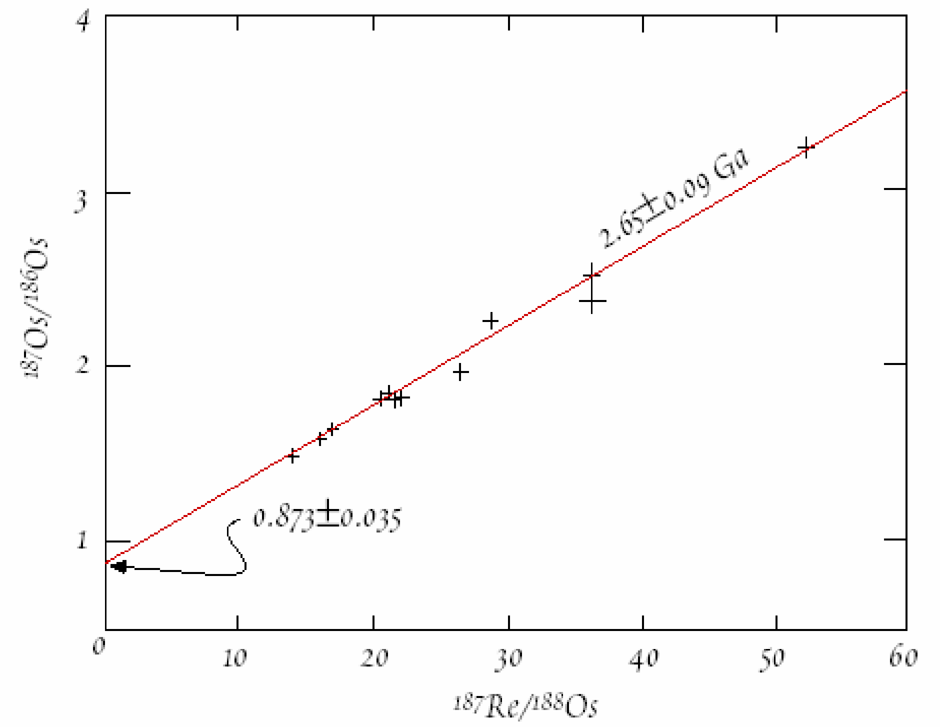
表 1 猫岭金矿毒砂的 Re-Os 分析结果

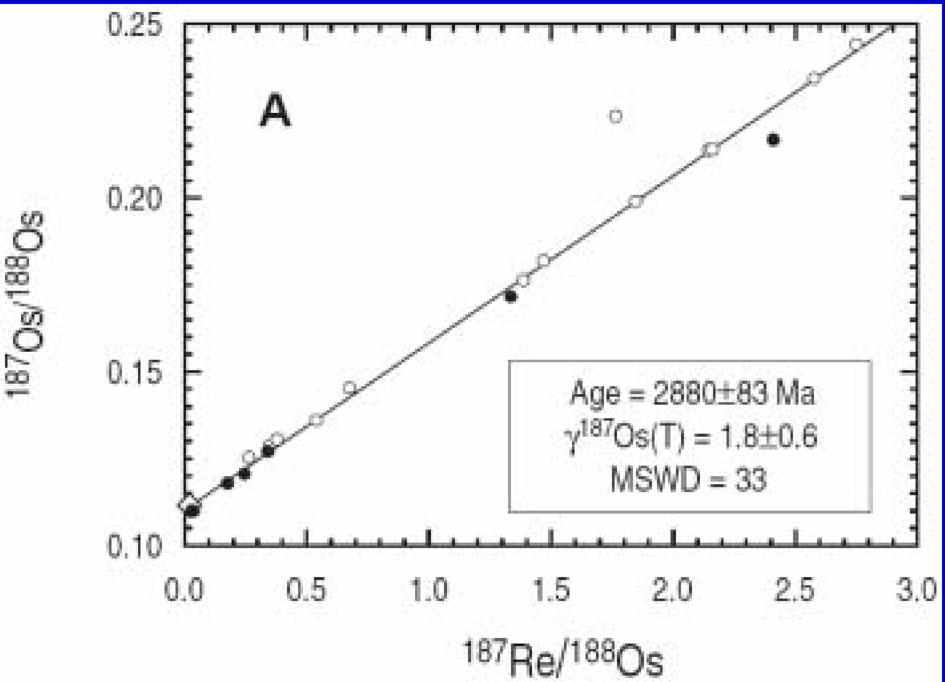
样品号	Re/10^{-9}g · g^{-1}	Os/10^{-9}g · g^{-1}	$^{187}Re/^{188}Os$	$^{187}Os/^{188}Os$	± [a]
01LN326	1.324	0.118	72.04	4.050	168
01LN327	0.834	0.0455	113.8	5.540	462
01LN329	6.406	0.210	530.3	21.73	66
duplicate	6.168	0.138	530.3	22.63	48
01LN331	0.864	0.0729	72.79	4.417	421
01LN334	3.192	0.188	146.3	7.218	168

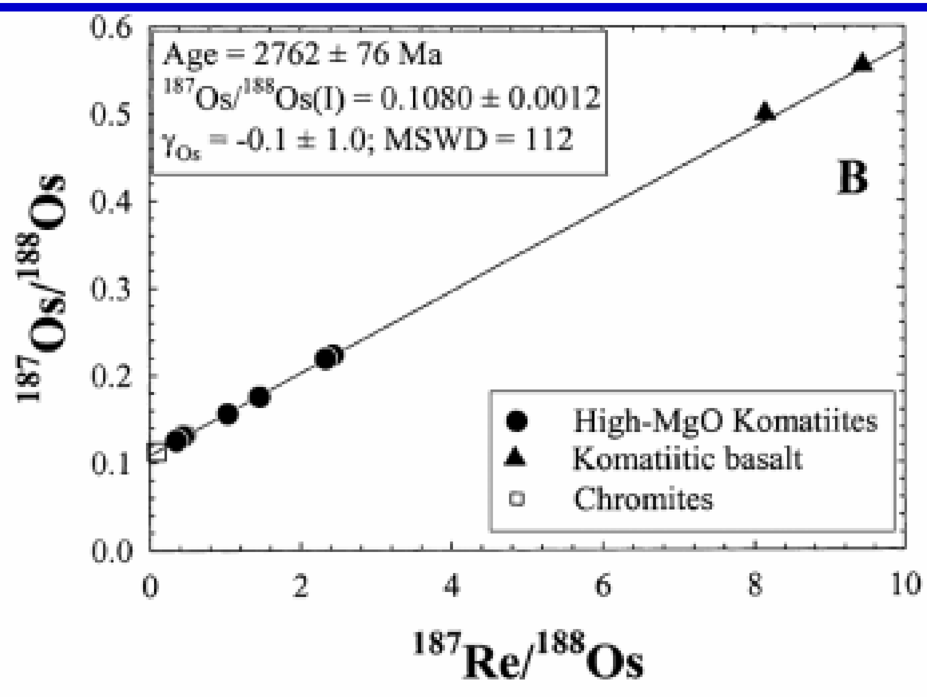
然而，对极低Re、Os含量的硫化物而言，准确年龄的获得对实验室的要求极高。

(4) 科马提岩定年

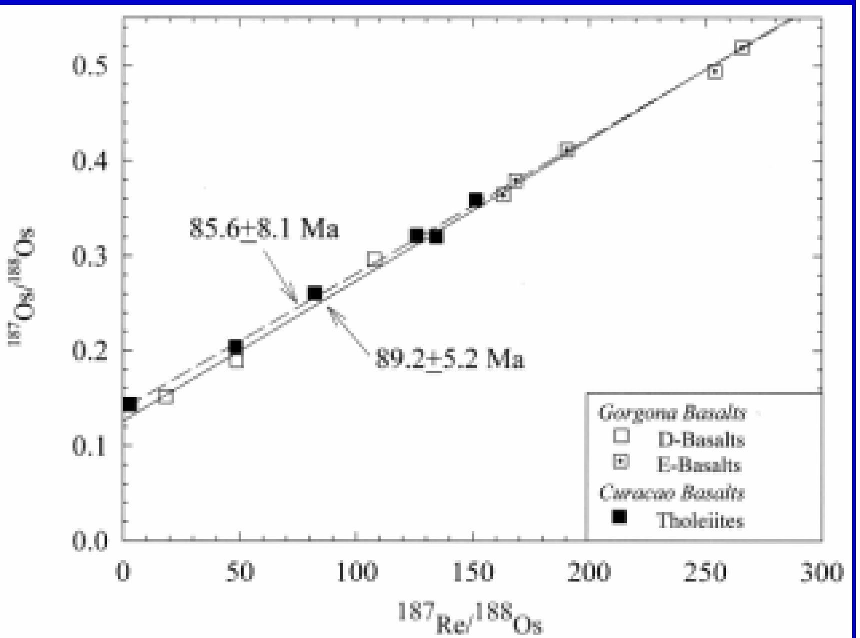
大多数情况下，科马提岩的准确定年仍是十分艰难！



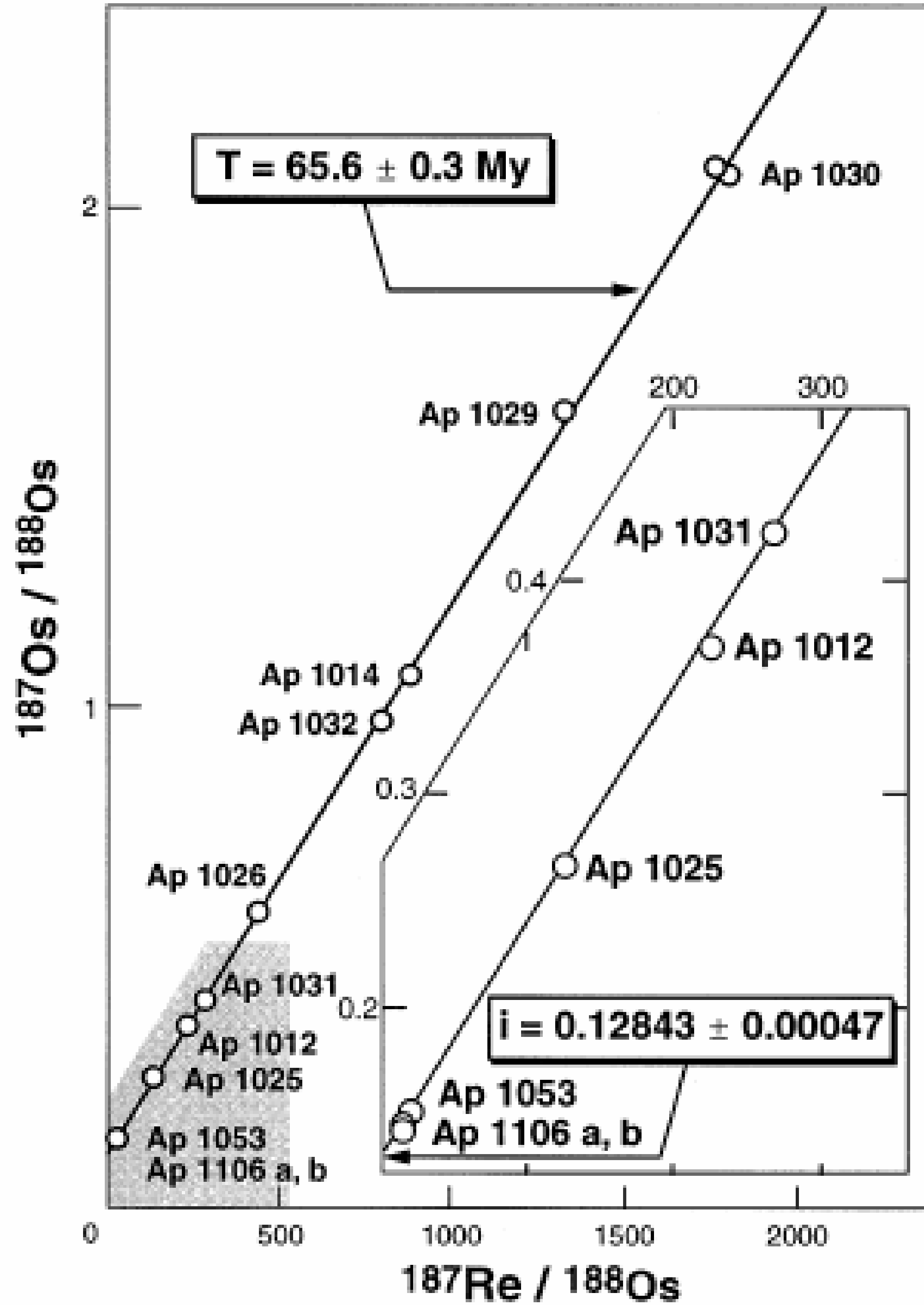




(4) 玄武岩定年

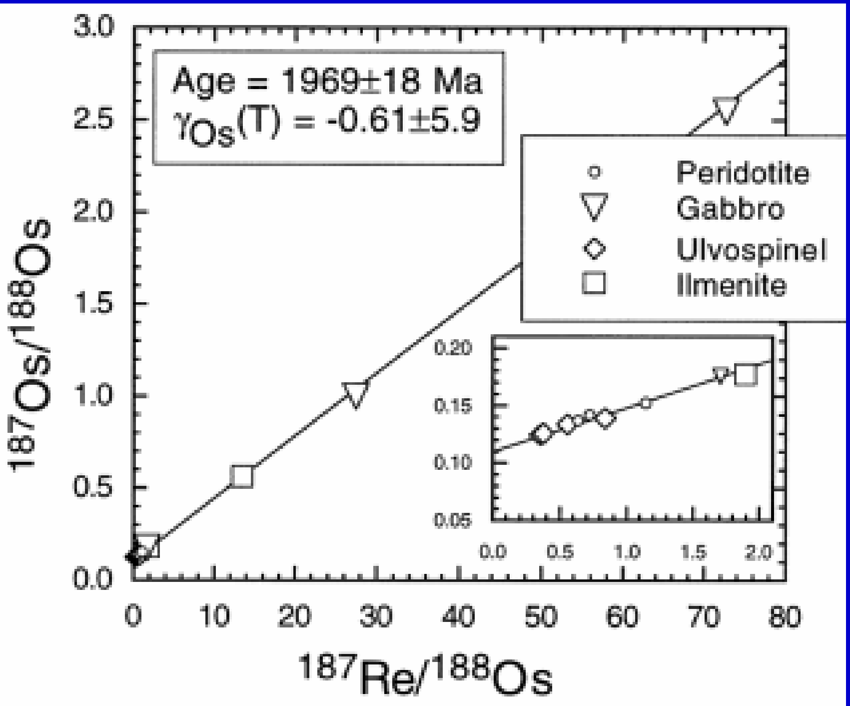


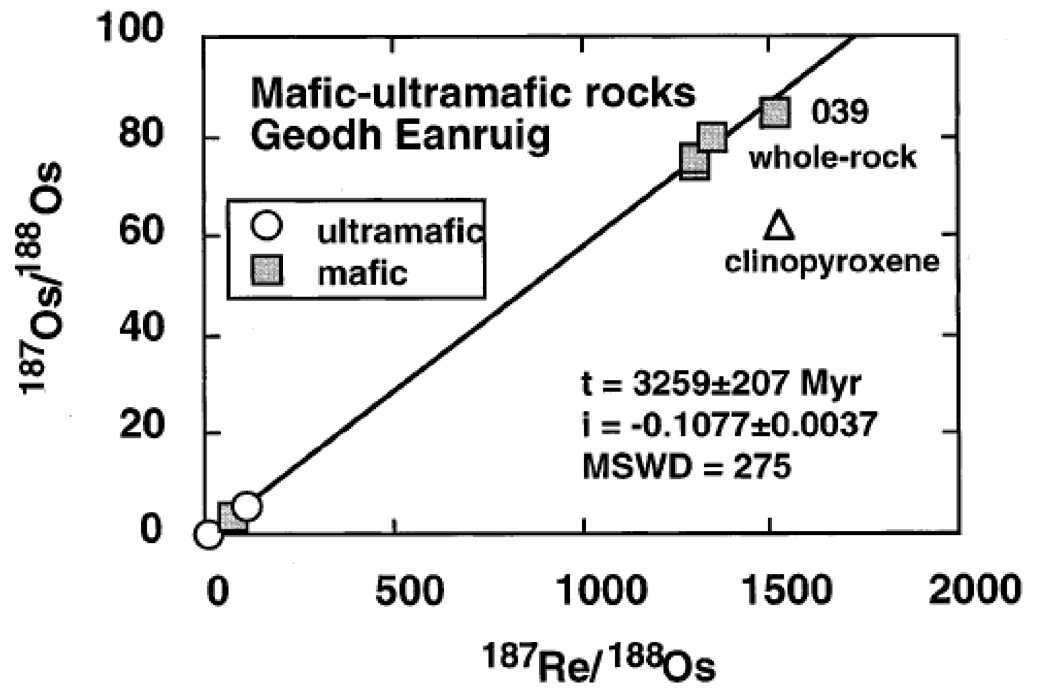
85.6±8.1 Ma
89.2±5.2 Ma
Gorgona Basalts
D-Basalts
E-Basalts
Curacao Basalts
Tholeiites
$^{187}Os/^{188}Os$
$^{187}Re/^{188}Os$



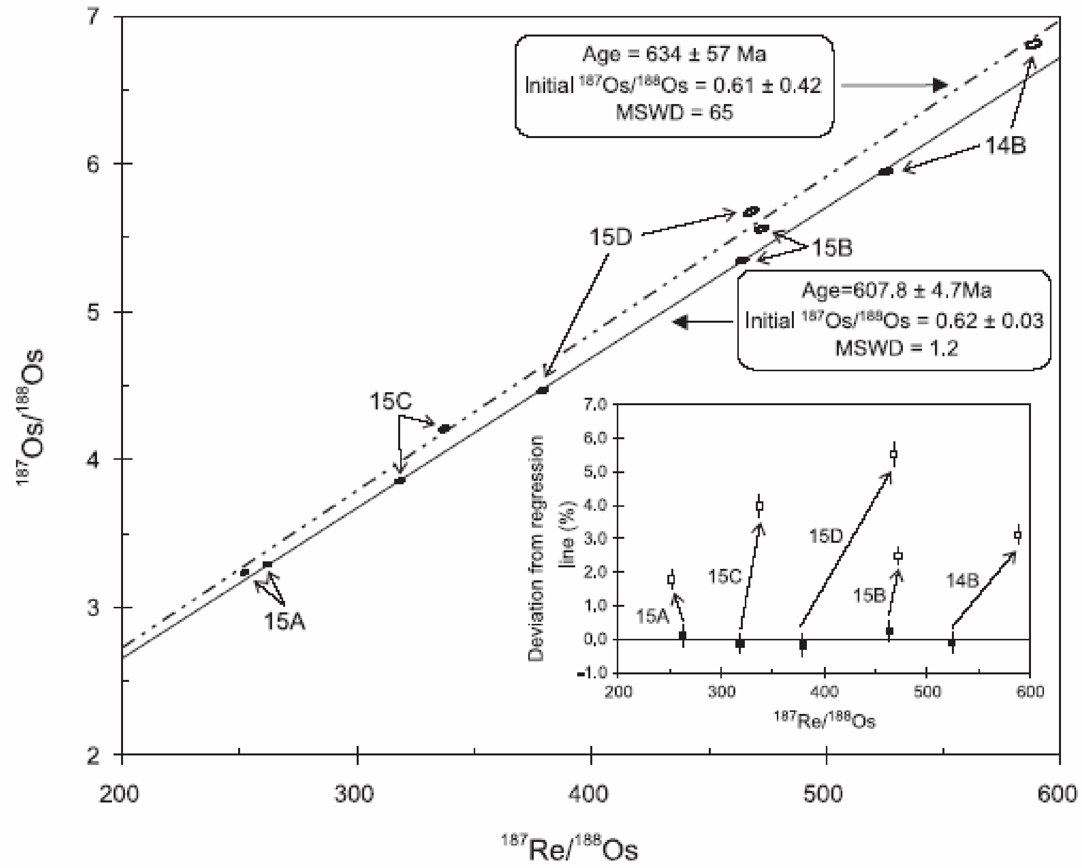
T = 65.6 ± 0.3 My
Ap 1030
Ap 1029
Ap 1014
Ap 1032
Ap 1026
Ap 1031
Ap 1012
Ap 1025
Ap 1053
Ap 1106 a, b
i = 0.12843 ± 0.00047
187Os / 188Os
187Re / 188Os

(5) 超镁铁-镁铁质侵入岩定年

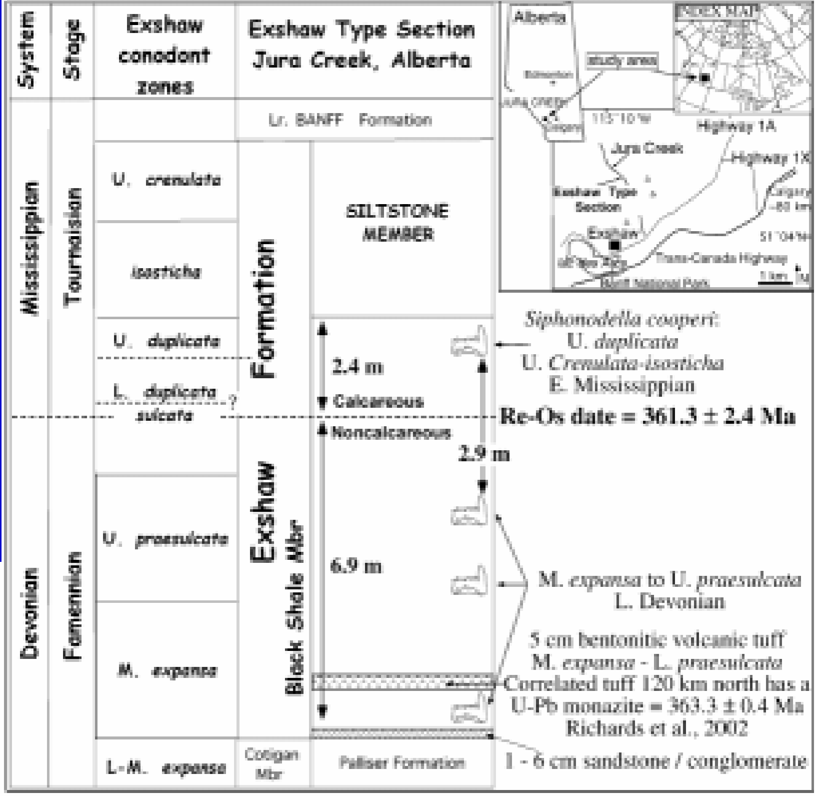




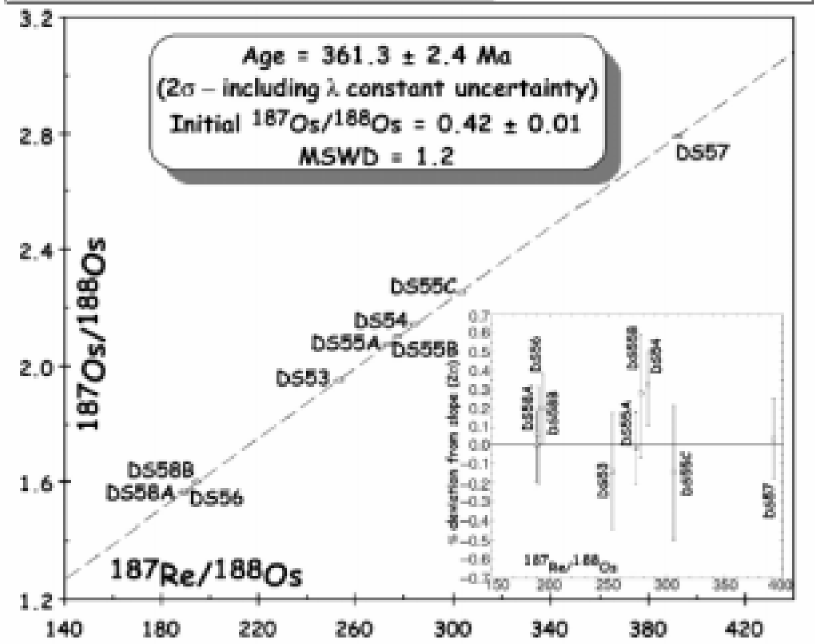
(6) 黑色页岩定年



Age = 634 ± 57 Ma
Initial $^{187}Os/^{188}Os$ = 0.61 ± 0.42
MSWD = 65
Age=607.8 ± 4.7Ma
Initial $^{187}Os/^{188}Os$ = 0.62 ± 0.03
MSWD = 1.2
14B
15D
15B
15C
15A
$^{187}Os/^{188}Os$
$^{187}Re/^{188}Os$
Deviation from regression line (%)



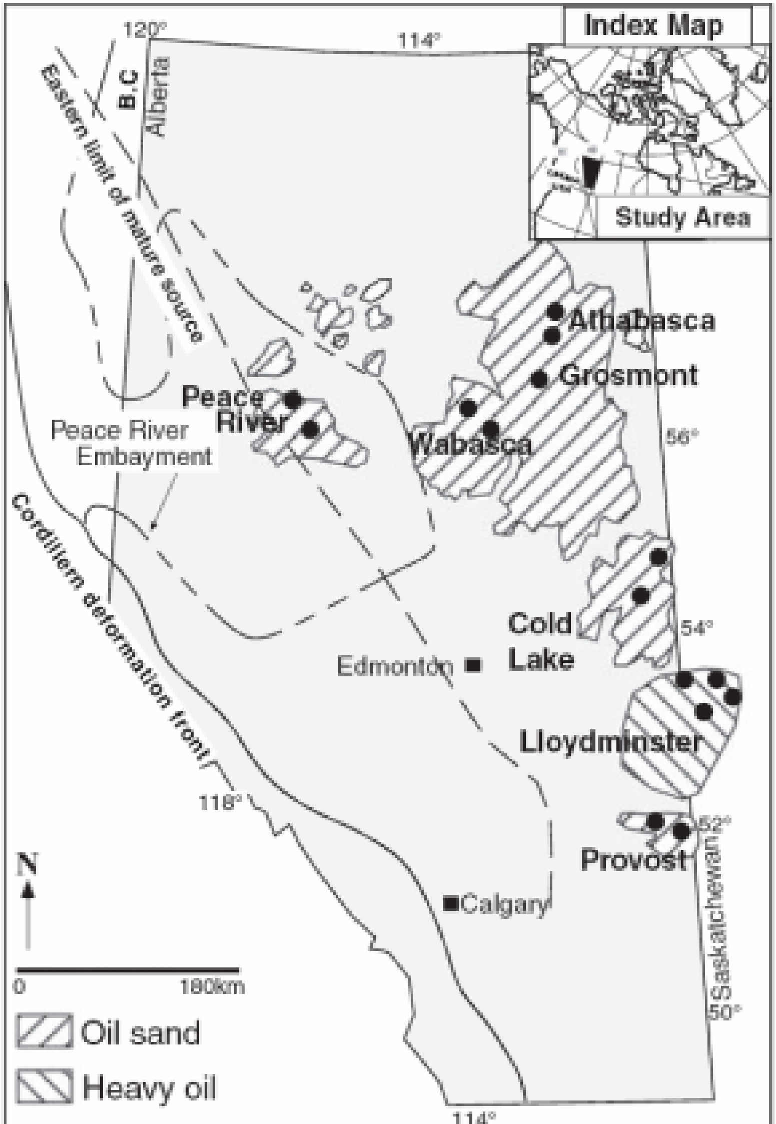
System
Stage
Exshaw conodont zones
Exshaw Type Section Jura Creek, Alberta
Lr. BANFF Formation
Mississippian
Tournaisian
Devonian
Famennian
U. crenulata
isosticha
U. duplicata
L. duplicata
sulcata
U. praesulcata
M. expansa
L-M. expansa
Exshaw Formation
SILTSTONE MEMBER
Black Shale Mbr
Cotigan Mbr
Palliser Formation
2.4 m
Calcareous
Noncalcareous
2.9 m
6.9 m
Siphonodella cooperi:
U. duplicata
U. Crenulata-isosticha
E. Mississippian
Re-Os date = 361.3 ± 2.4 Ma
M. expansa to U. praesulcata
L. Devonian
5 cm bentonitic volcanic tuff
M. expansa - L. praesulcata
Correlated tuff 120 km north has a
U-Pb monazite = 363.3 ± 0.4 Ma
Richards et al., 2002
1 - 6 cm sandstone / conglomerate
Alberta
INDEX MAP
study area
Highway 1A
Jura Creek
Highway 1X
Exshaw Type Section
Exshaw
Trans-Canada Highway
Banff National Park

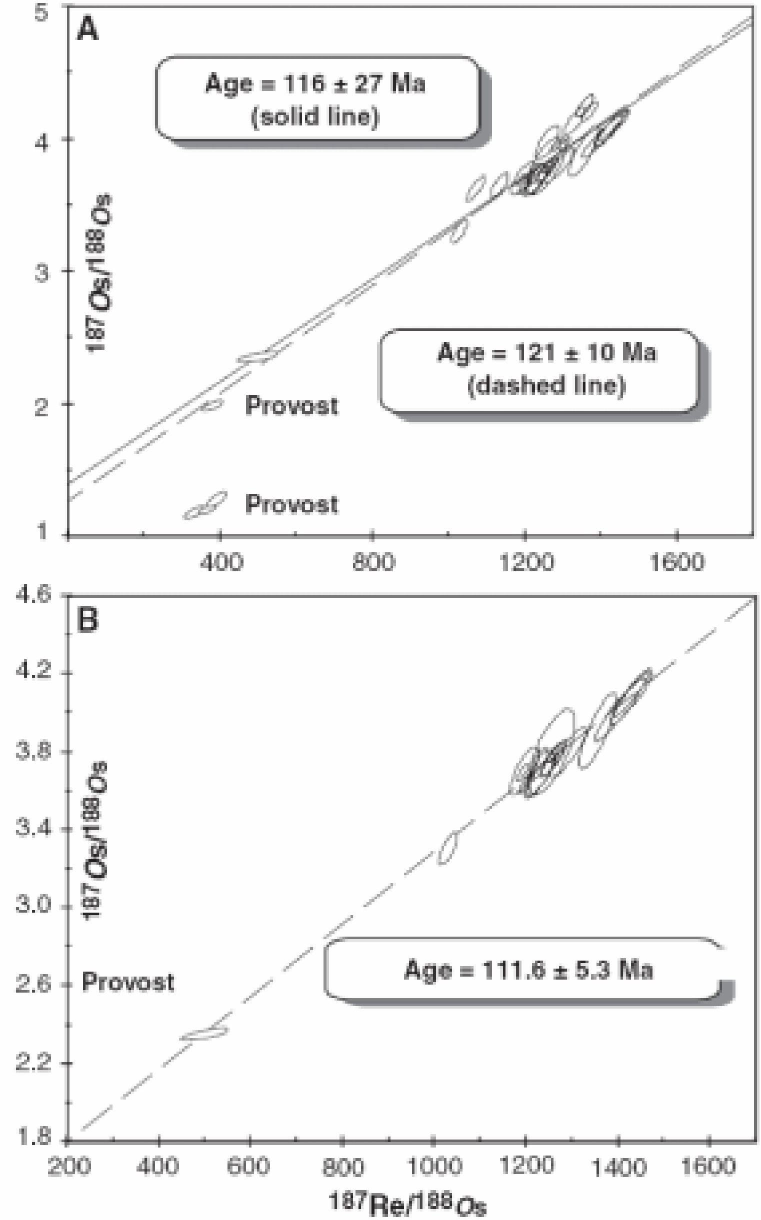


Age = 361.3 ± 2.4 Ma
(2σ – including λ constant uncertainty)
Initial $^{187}Os/^{188}Os$ = 0.42 ± 0.01
MSWD = 1.2
DS57
DS55C
DS54
DS55A
DS55B
DS53
DS58B
DS58A
DS56
187Os/188Os
187Re/188Os

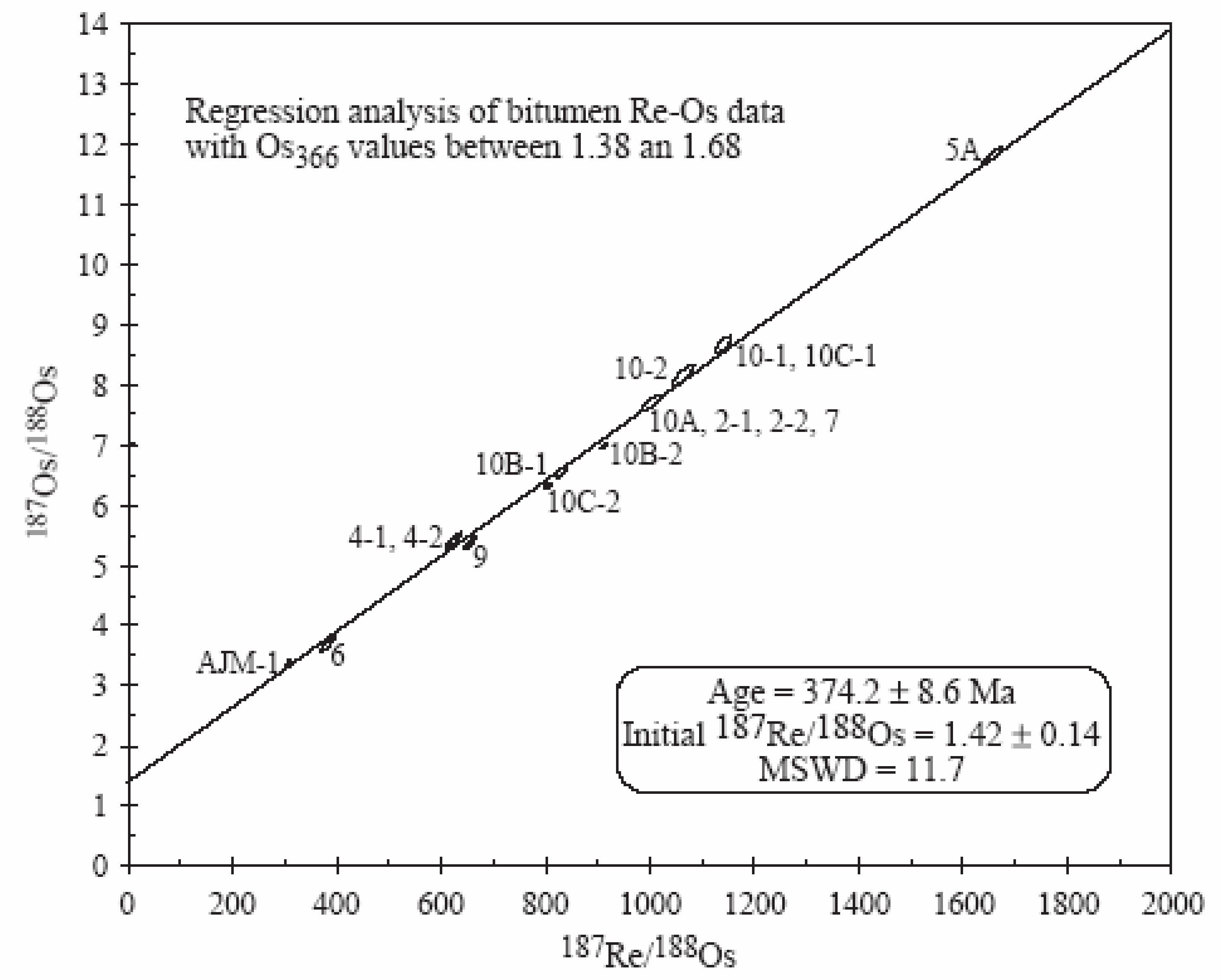
(7) 有机物形成年龄（Sleby et al., 2005a）

Fig. 1 (left). Location map of the Alberta oil sand deposits. Black circles mark the sample locations. Fig. 2 (right). Re-Os isochron diagrams for the Alberta oil sand oil. (A) Regression of Re-Os data, not including that for Provost, yields a model 3 Re-Os date of 116 ± 27 Ma ($n = 24$, MSWD = 21, 2σ uncertainty) with an initial $^{187}Os/^{188}Os$ ratio of 1.40 ± 0.56 (solid line). By including Provost samples 1418 and 1431, an Re-Os date of 121 ± 10 Ma ($n = 26$, MSWD = 21, 2σ uncertainty, model 3) with an initial $^{187}Os/^{188}Os$ ratio of 1.29 ± 0.21 is determined (dashed line). (B) Seventeen samples have Os_{110} values of 1.4 to 1.5, which yield a date of 111.6 ± 5.3 Ma (MSWD = 2.2, model 3), with an initial $^{187}Os/^{188}Os$ ratio of 1.43 ± 0.11 (20).

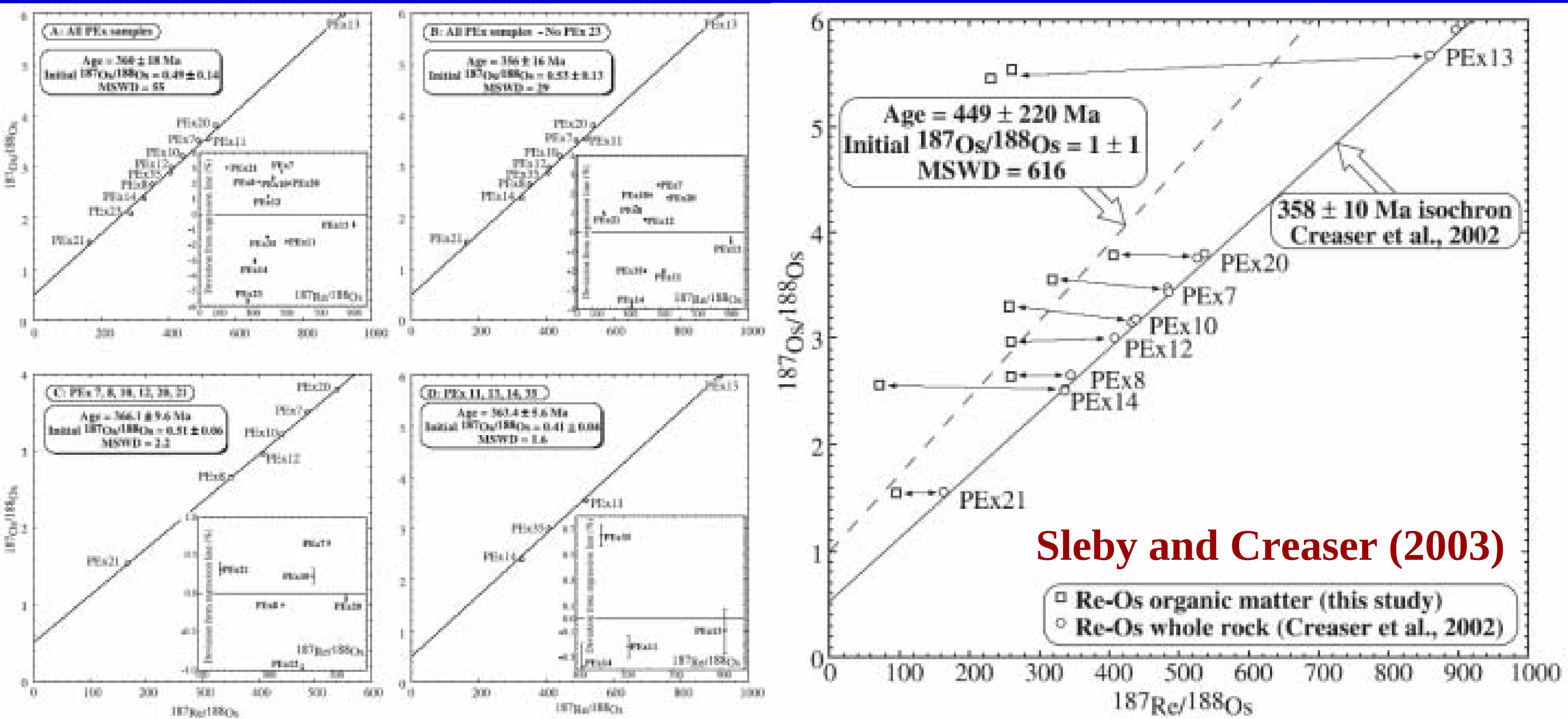




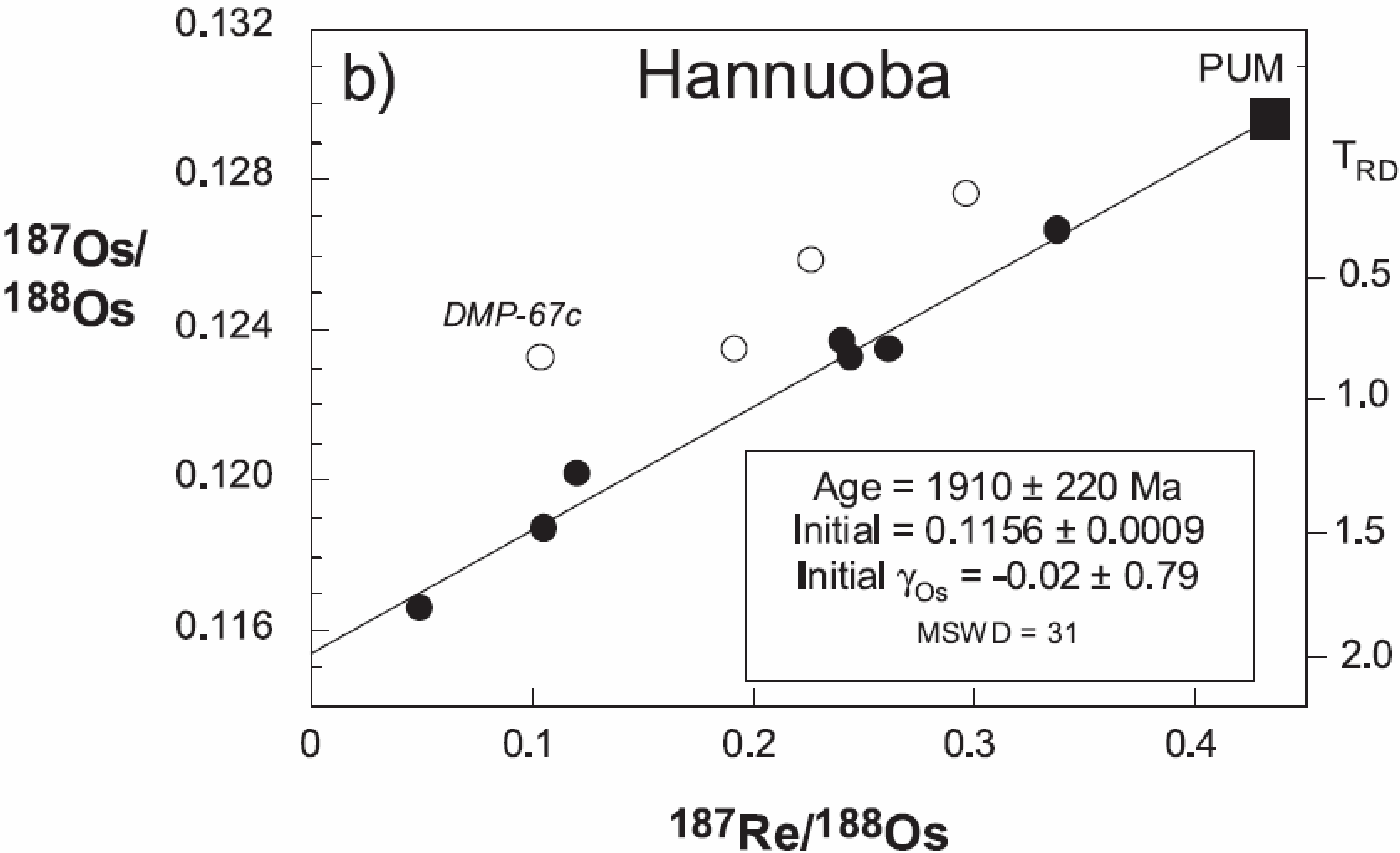
有机物形成年龄（Sleby et al., 2005b）



但有机物的定年需要克服其中非有机物的干扰



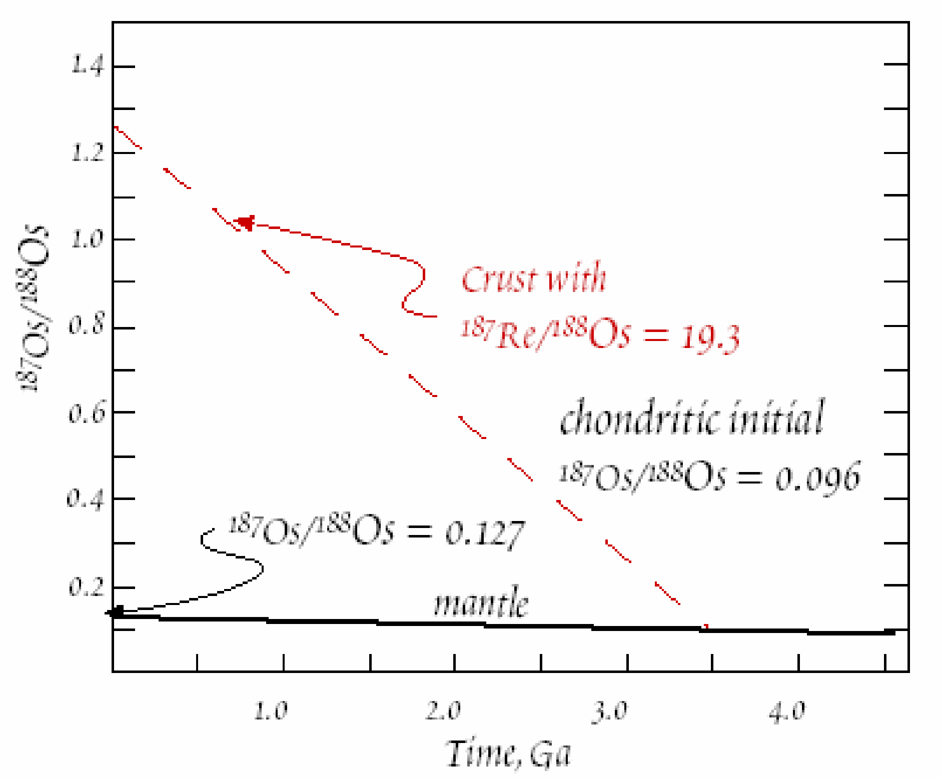
(8) 岩石圈地幔定年（Gao et al., 2002）

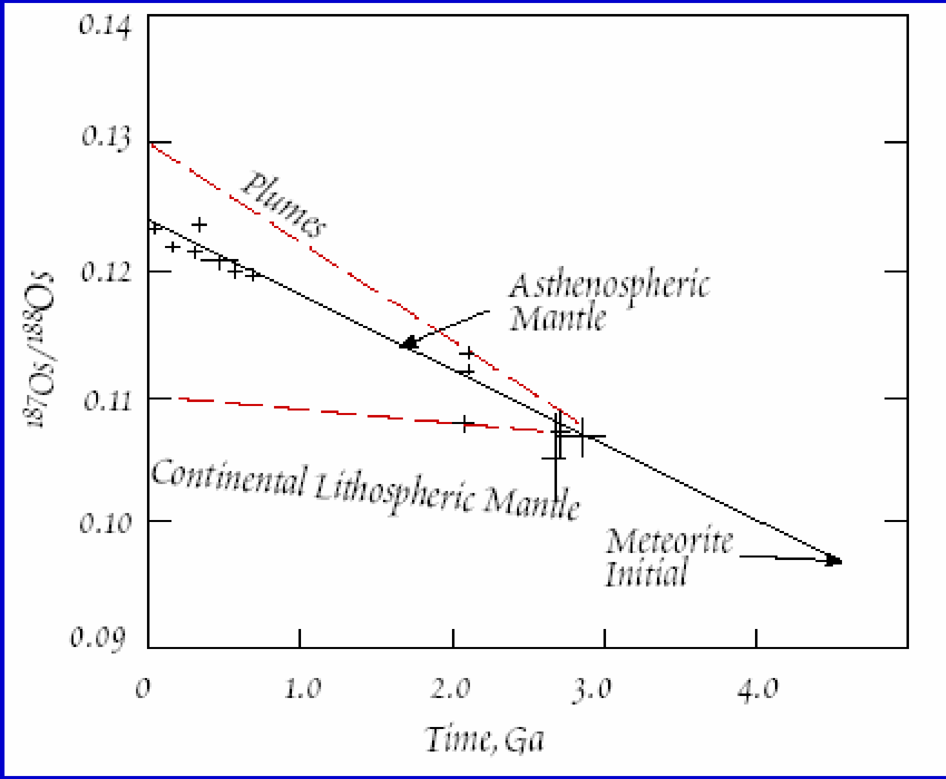


4. Re-Os 同位素地球化学

The siderophile/chalcophile nature of Re and Os makes this isotope system useful to address questions of core formation and ore genesis.

Unlike other radioactive and radiogenic elements, which are incompatible ones and hence enriched in melts, Os is a highly compatible element (bulk D ~ 10) and is enriched in the residual solid. This makes Os isotope ratios particularly useful in studies of the crust-mantle evolution.



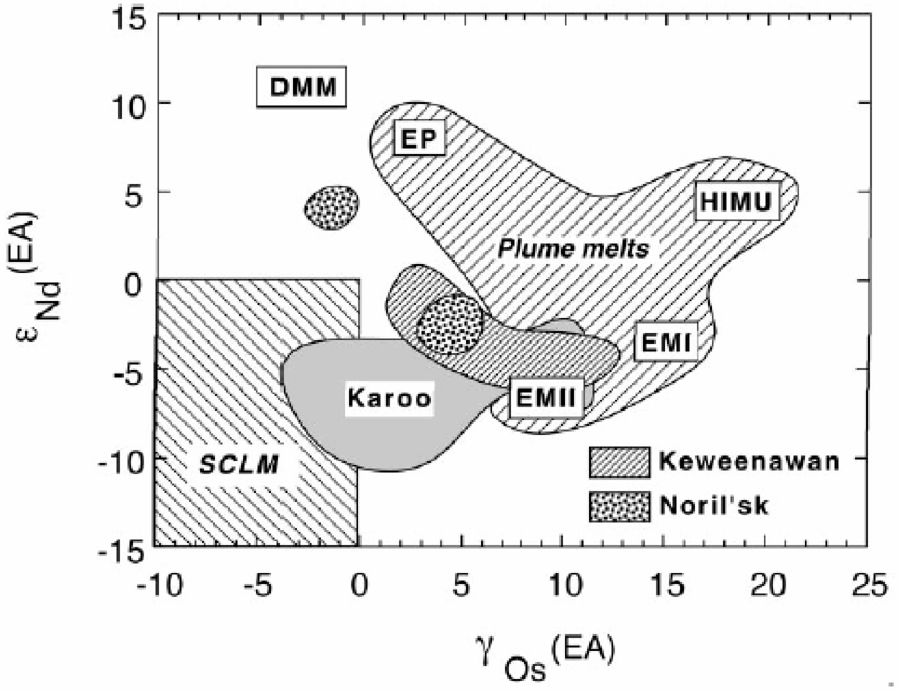


Schematic evolution of Os isotope ratios in the mantle and crust.

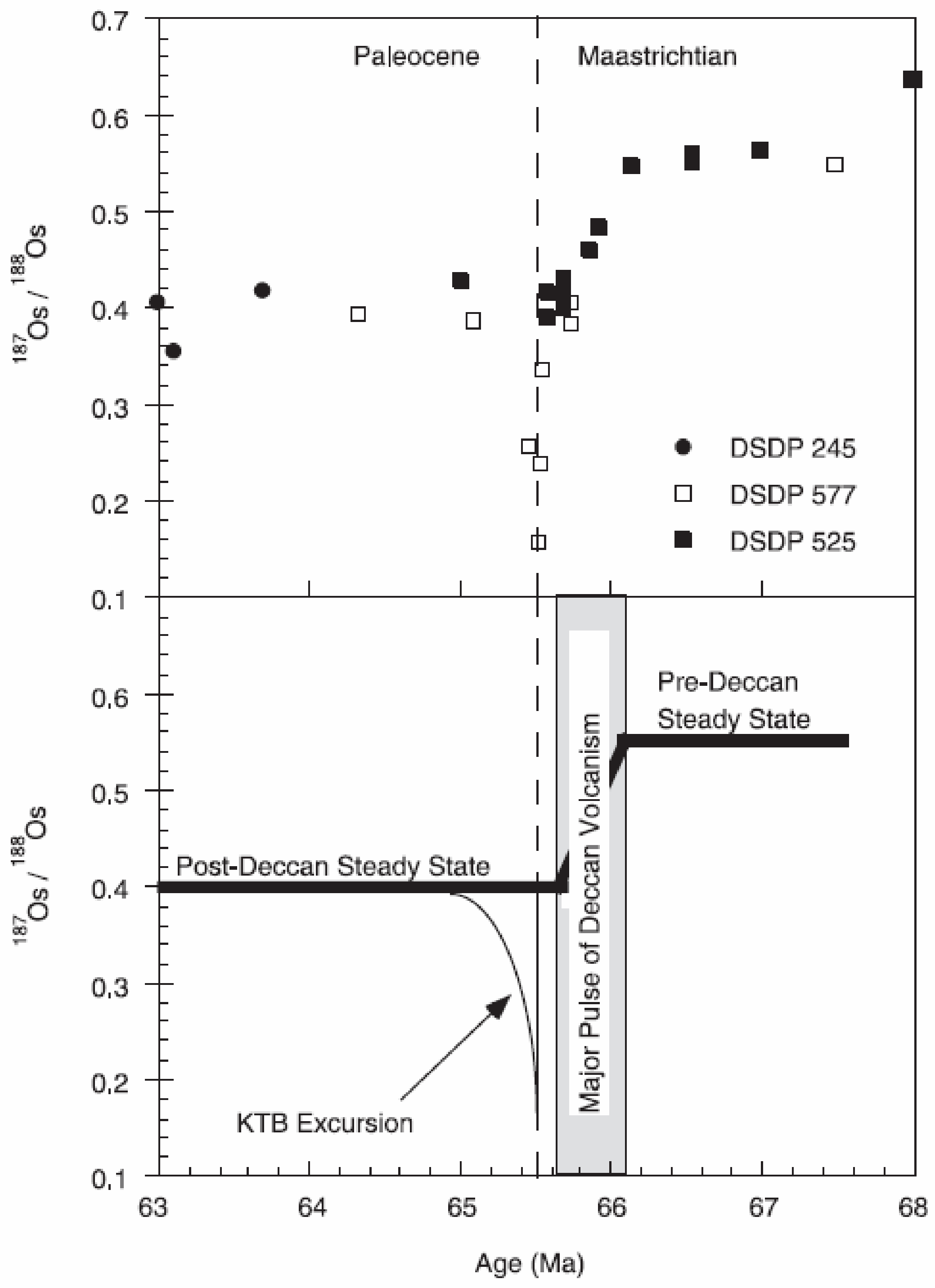
Table 3 $^{187}Os/^{188}Os$ and γ_{Os} of various terrestrial mantle reservoirs

Reservoir	$^{187}Os/^{188}Os$	γ_{Os}
Fertile convecting mantle		
Chondritic reference	0.127	0.0
PUM (primitive upper mantle)	0.129	+1.6
SCLM (subcontinental lithospheric mantle)		
Average	0.113	−11.0
Range	0.105–0.129	−17.3 to +1.6
DMM (depleted MORB mantle)[a]		
Average	0.125	−1.9
Range	0.123–0.126	−3.1 to −0.8
EP (enriched plume end member, FOZO?)	0.130–0.135	+2.4 to +6.3
HIMU (high μ)	0.150	+18.1
EM I (enriched mantle I)	0.152	+19.7
EM II (enriched mantle II)	0.136	+7.1

[a]Based on abyssal peridotites.

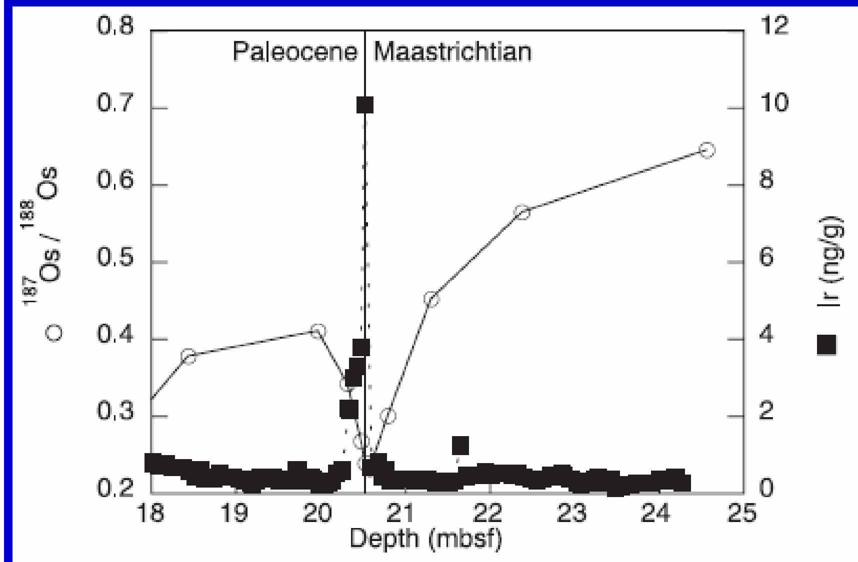


重要地球化学储库的Os同位素特征（Shirey and Walker, 1998）



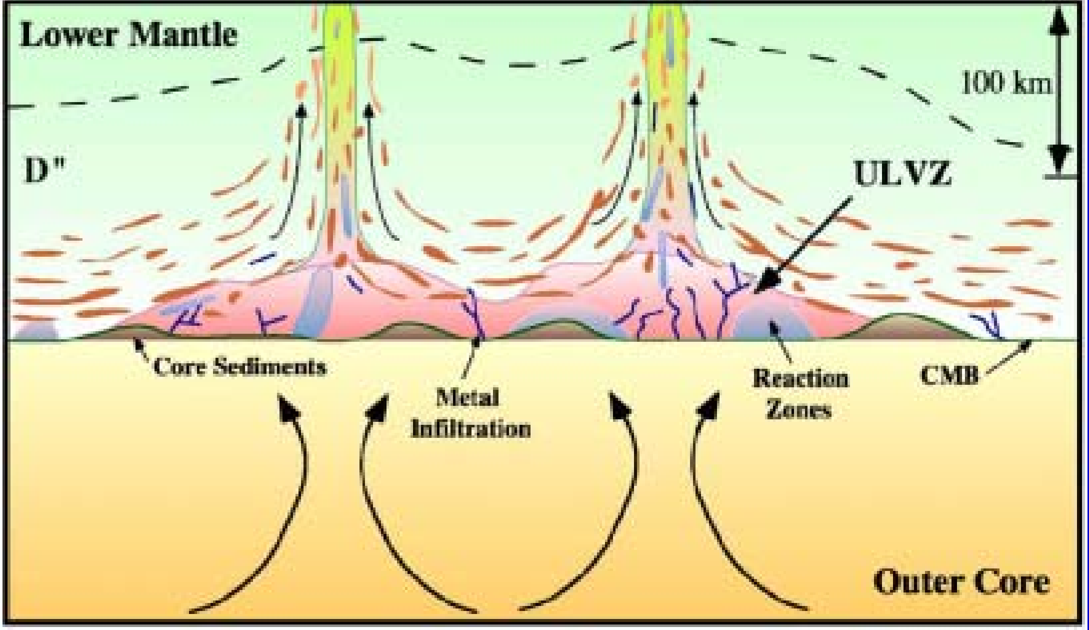
K/T边界的性质

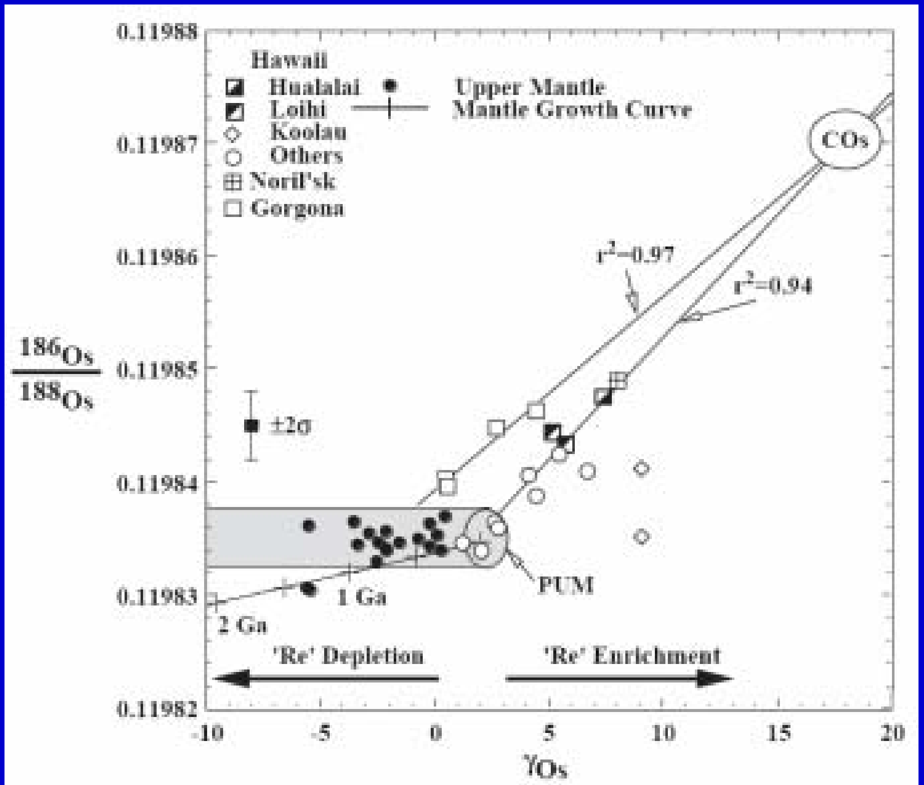
(Ravizz and Peucker-Ehrenbrink, 2003)

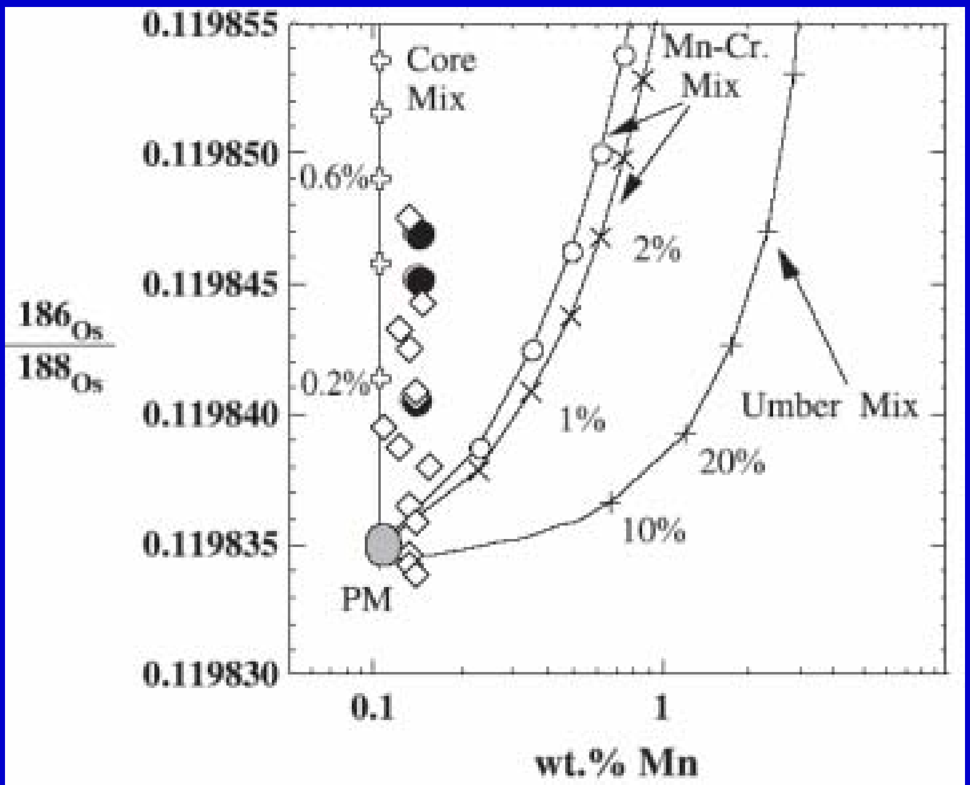


地幔柱来自核幔边界吗？

(Brandon and Walker, 2005)







地幔Os同位素定年基本原理

1）**Re**为不相容元素，但**Os**为相容元素，因而后者在地幔中含量较高；

2）由于**Re**较易进入熔体，从而使地幔在熔体抽取形成岩石圈地幔后亏损**Re**，而熔体抽取程度的不同可造成源区**Re/Os**比值不同。

如何定义岩石圈地幔的年龄？

Subcontinental Lithospheric mantle is the residue of fertile mantle by removal of partial melt (basaltic), and represents the chemical complement to the incompatible-element-enriched continental crust.

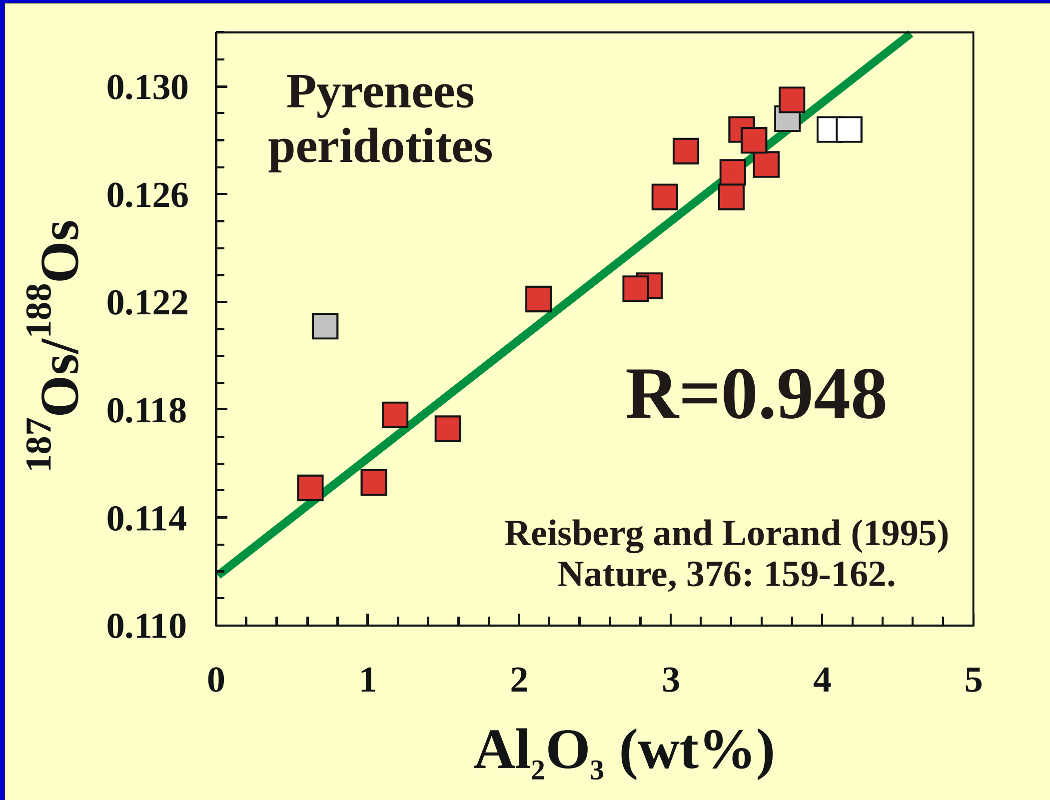
Separation time from the convecting mantle，coeval to the overlying crust.

The main drawback of Re-Os method:

The Re mobility makes the $^{187}Re/^{188}Os$ ratio, sometimes, unreasonable. Hence, no isochron could be obtained in this case.

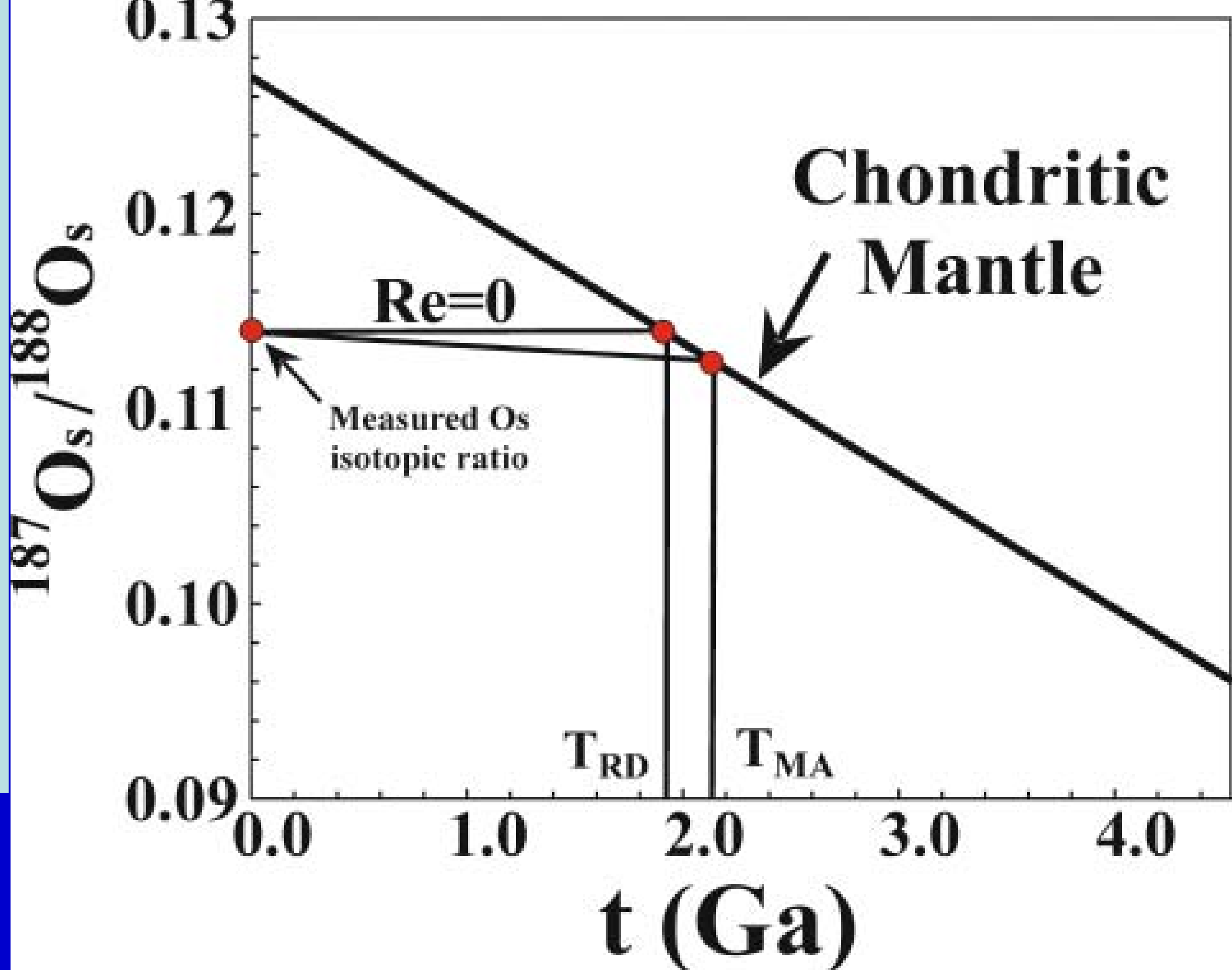
Alumichron method

(Reisberg and Lorand, 1995)



由于Re具有一定的活动性，使得等时线方法往往不能奏效，因而目前多采用模式年龄和代用等时线两种方法。

Walker et al., 1989. GCA, 53: 1583-1595.



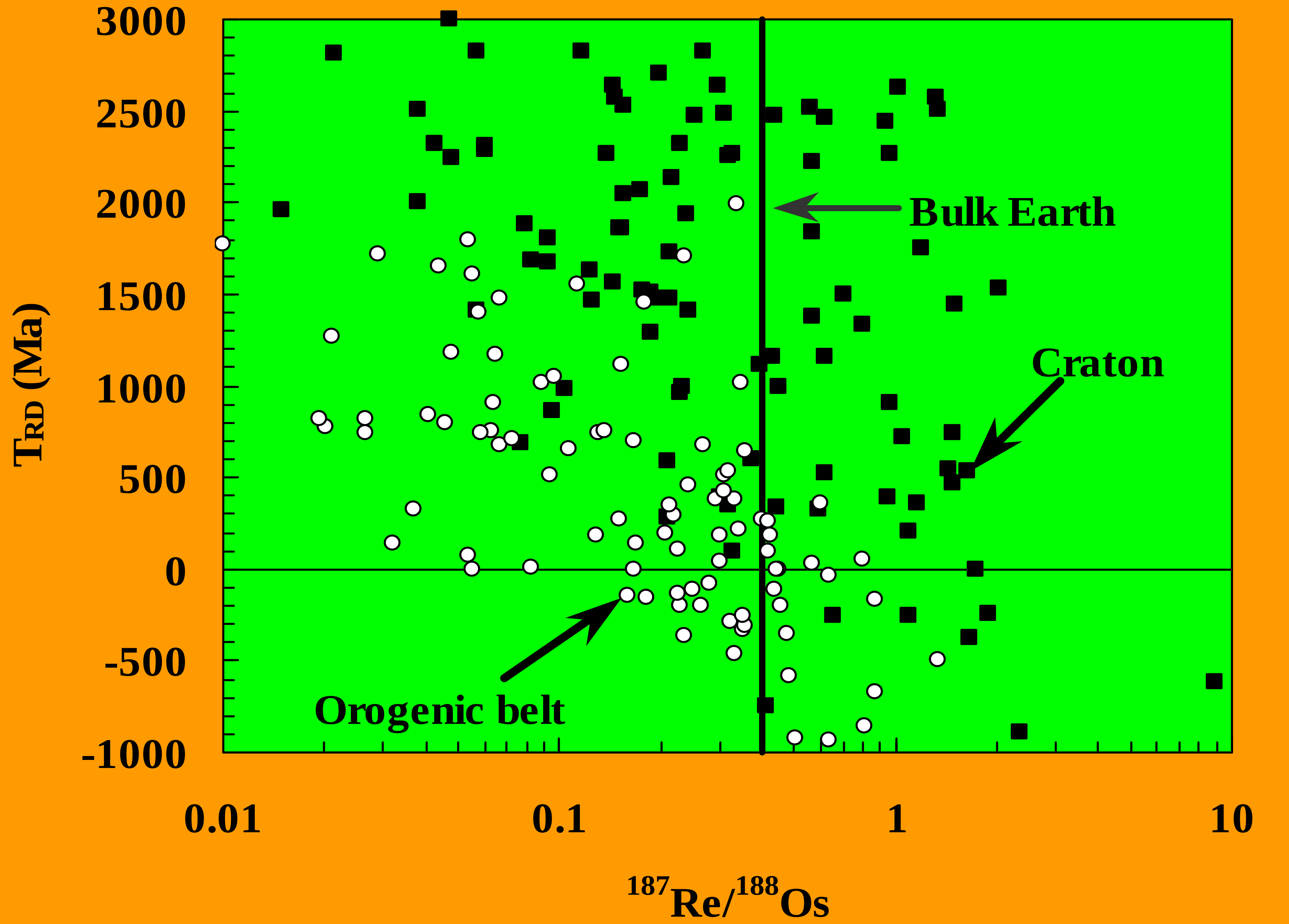
$$T_{MA} = 1/\lambda \times \ln\{[(^{187}Os/^{188}Os_{chon} - {}^{187}Os/^{188}Os_{sample})/(^{187}Re/^{188}Os_{chon} - {}^{187}Re/^{188}Os_{sample})] + 1\}.$$

$$T_{RD} = 1/\lambda \times \ln\{[(^{187}Os/^{188}Os_{chon} - {}^{187}Os/^{188}Os_{sample(EA)})/{}^{187}Re/^{188}Os_{chon}] + 1\},$$

Advantages of the Os isotopic technique:

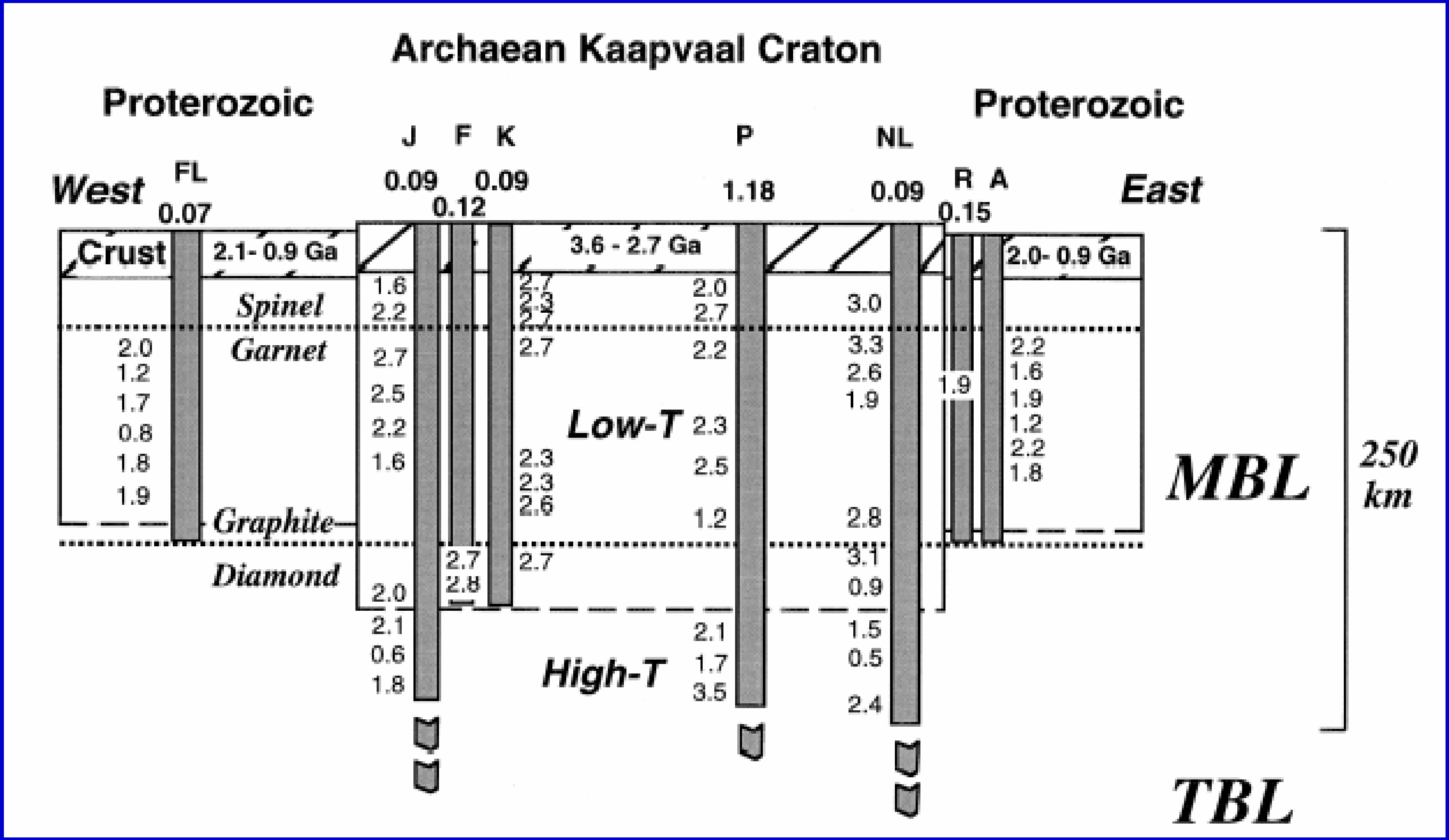
1) Contaminations from host magma, crustal rocks and mantle metasomatism are ignorable because of the high Os concentration of mantle peridotites.

2) For harzburgite, T_{RD} could approach the true SCLM age due to its low Re concentration and Re/Os ratio.



3000
2500
2000
1500
1000
500
0
-500
-1000
T_{RD} (Ma)
0.01
0.1
1
10
$^{187}Re/^{188}Os$
Bulk Earth
Craton
Orogenic belt

岩石圈地幔定年取得的主要成就

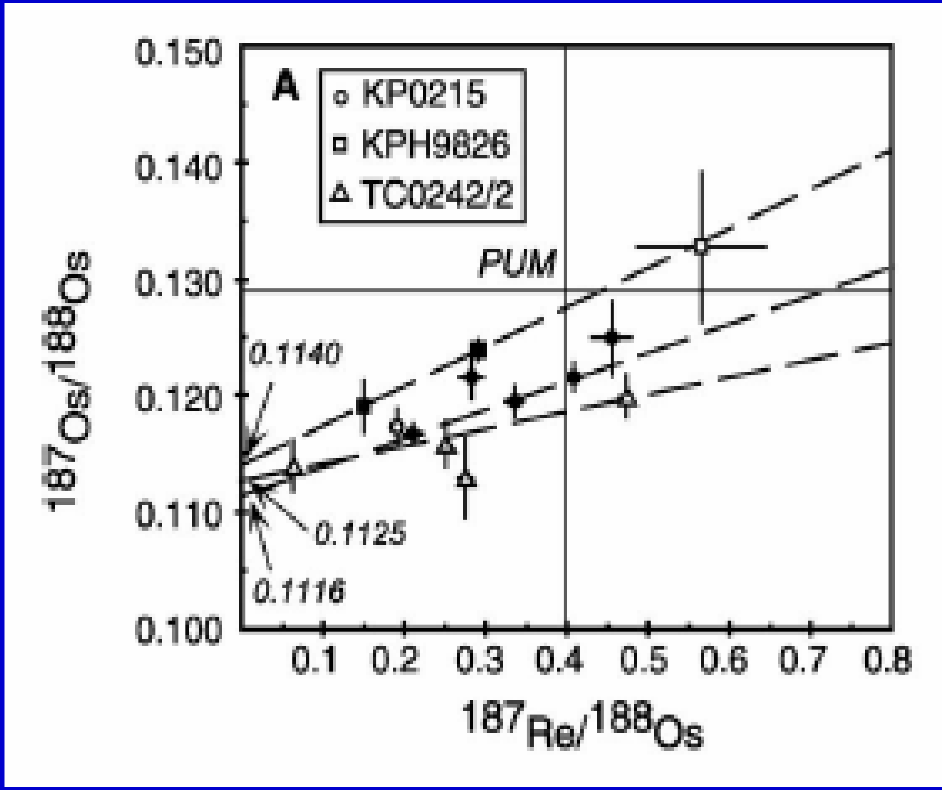


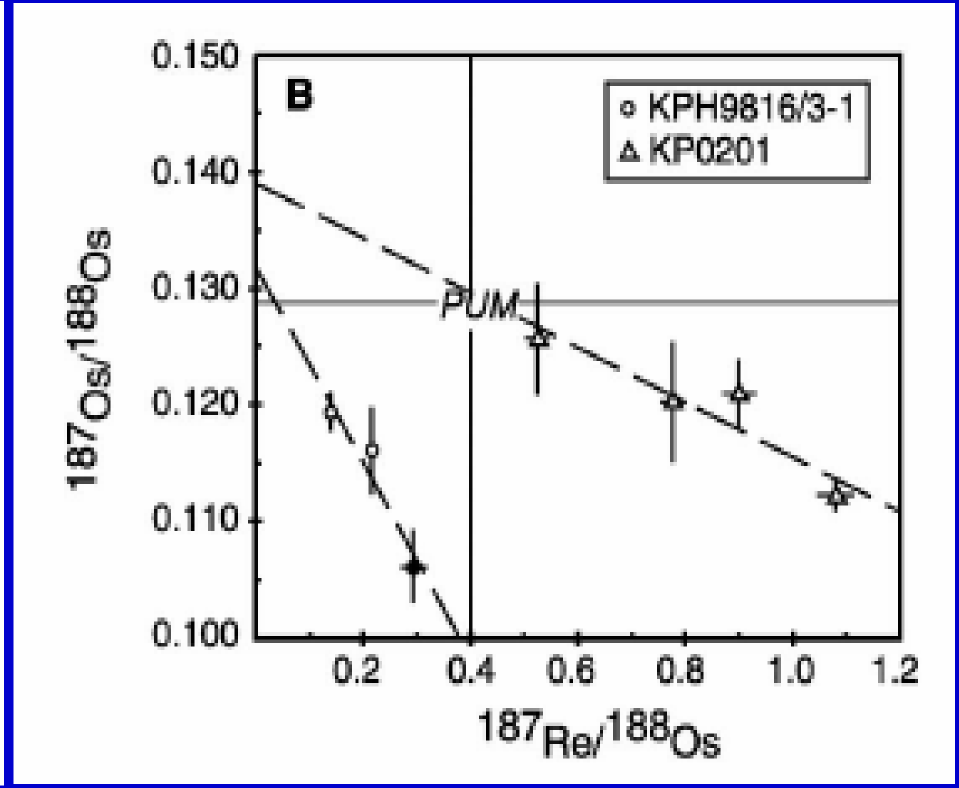
岩石圈地幔与上覆地壳的年龄基本一致，从而表明壳幔是耦合的，这也符合经典的板块构造模式和壳幔演化的理论模型。

一个潜在的问题是，上述全岩方法有可能掩盖多期事件的存在，因而目前部分学者倡导微区硫化物的激光定年，并发现粒内和粒间硫化物的年龄（及化学成分）存在明显差别，但对所获得的结果目前争议较大。

Alard et al., 2000. Nature, 407: 891-894.
Alard et al., 2002. EPSL, 203: 651-663.
Pearson et al., 2002. GCA, 66: 1037-1050.
Griffin et al., 2002. G^3,
Wang et al., 2003. Geology, 709-712.

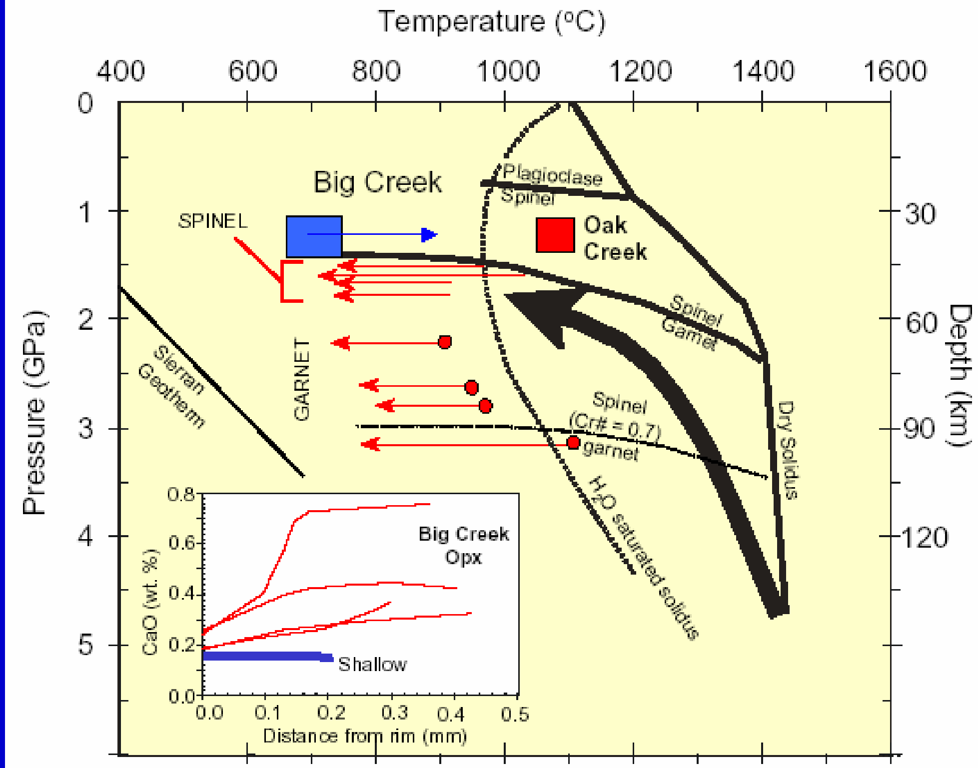
是等时线还是混合线？

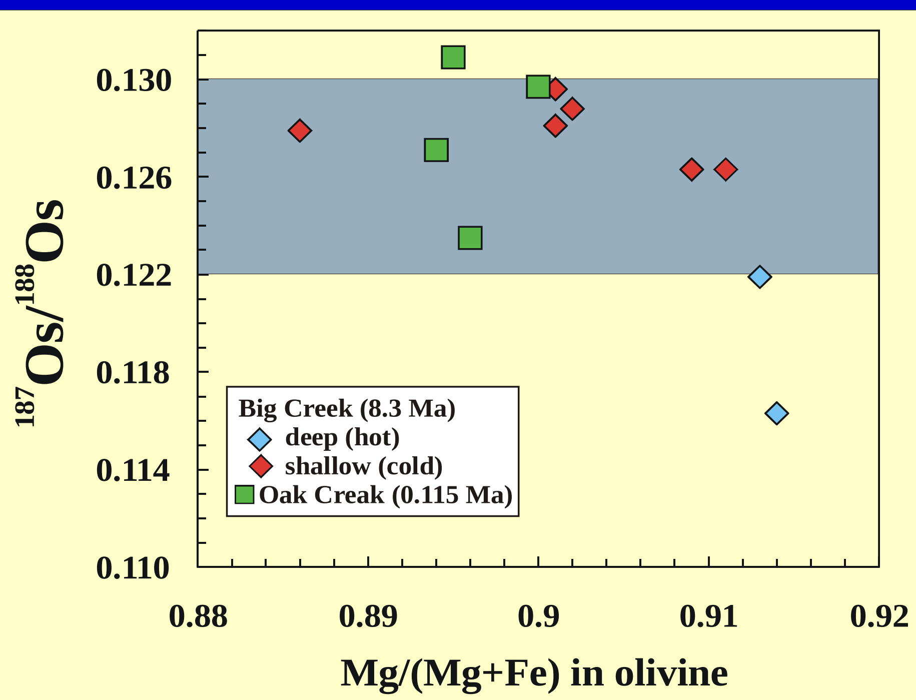


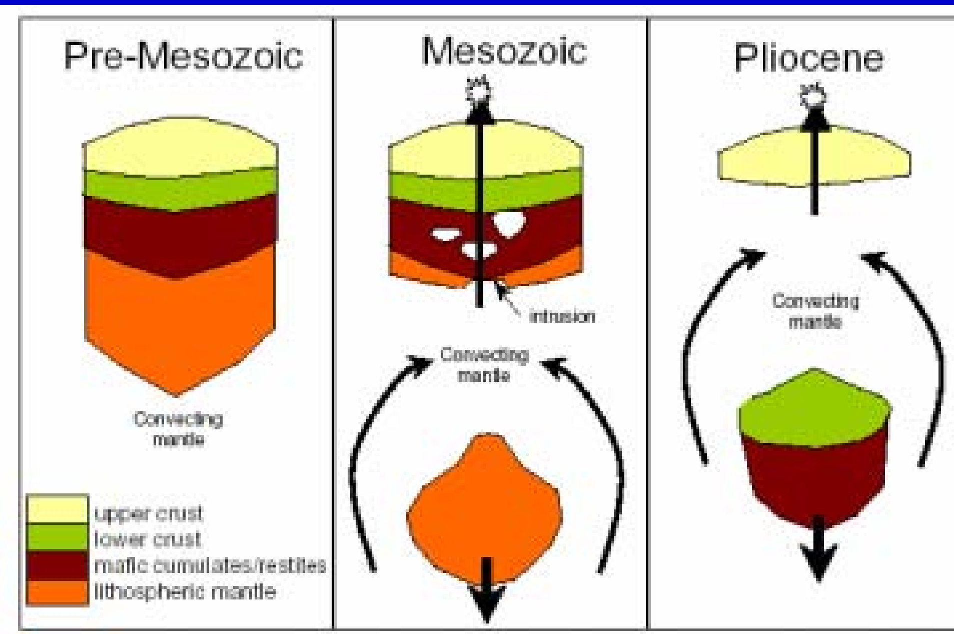


Wang et al., 2003. Geology, 709-712.

美国西部新生代岩石圈演化
(Lee et al., 2001a, 2001b)



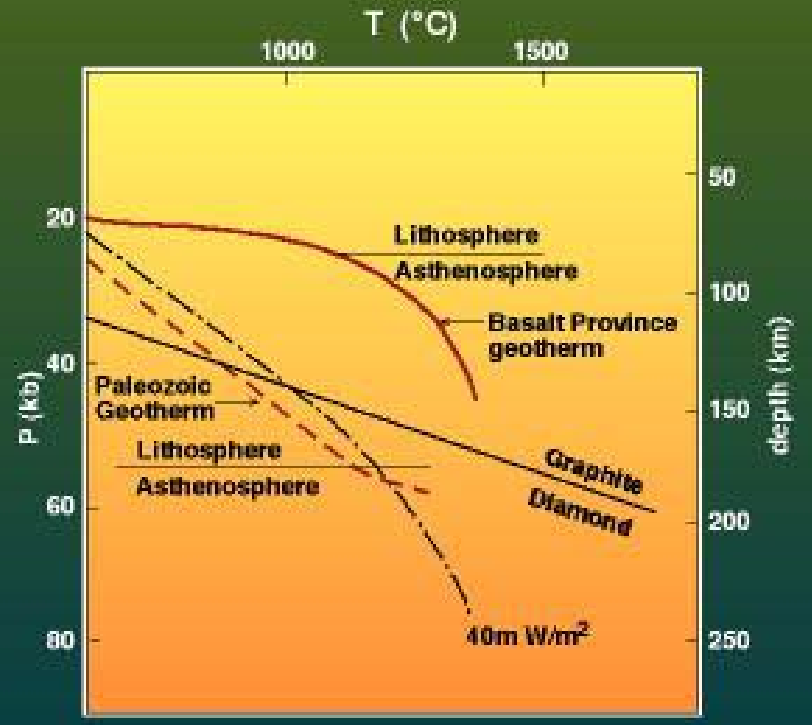




中国东部岩石圈地幔的 Re-Os同位素研究

Lithospheric thickness of the NCC in the Phanerozoic

- **Paleozoic kimberlites**
  - ~200 km
- **Present lithosphere**
  - 60-80 km
    - Geophysical data
    - Constraint from Cenozoic basalts and their mantle xenoliths
- **Loss of >100 km SCLM in Phanerozoic**

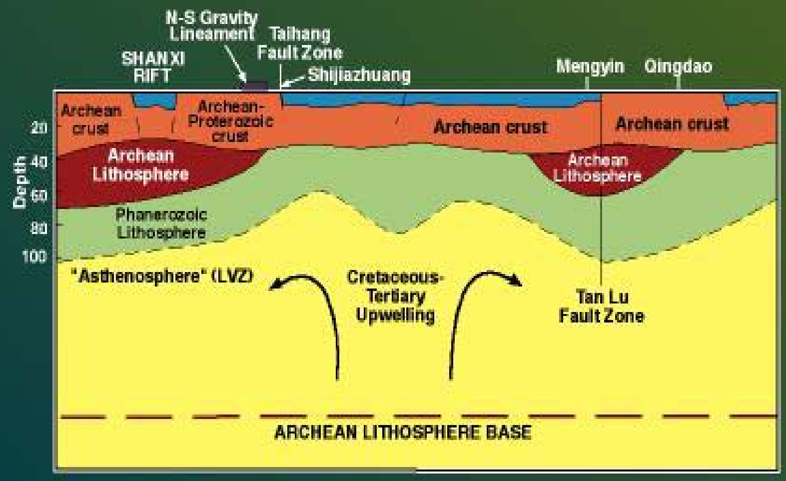


(Griffin et al., 1998)

Science of the NCC:

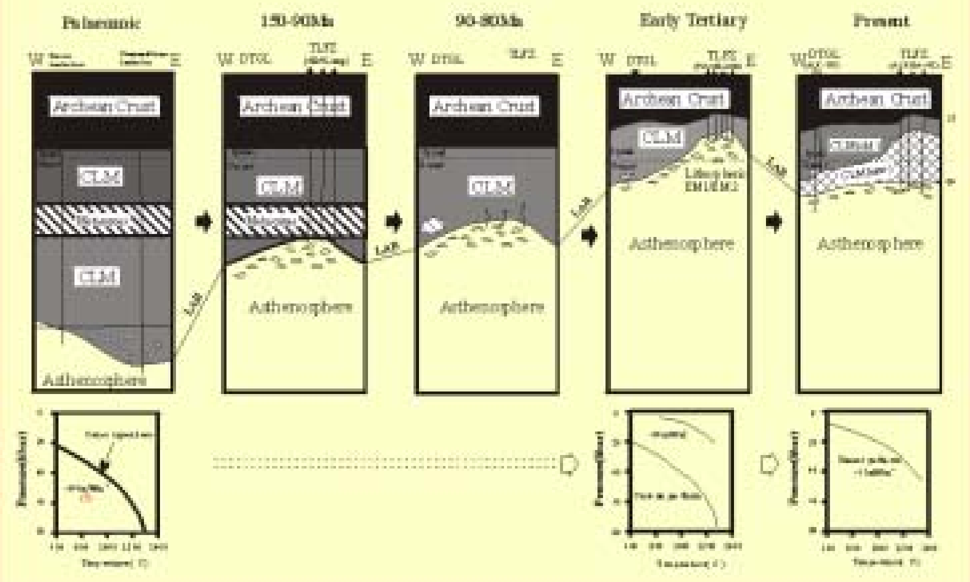
Why ancient continental root could be destroyed and lost?

- How much of the root was lost?
- When did this loss occur?
- Why and how was it lost?



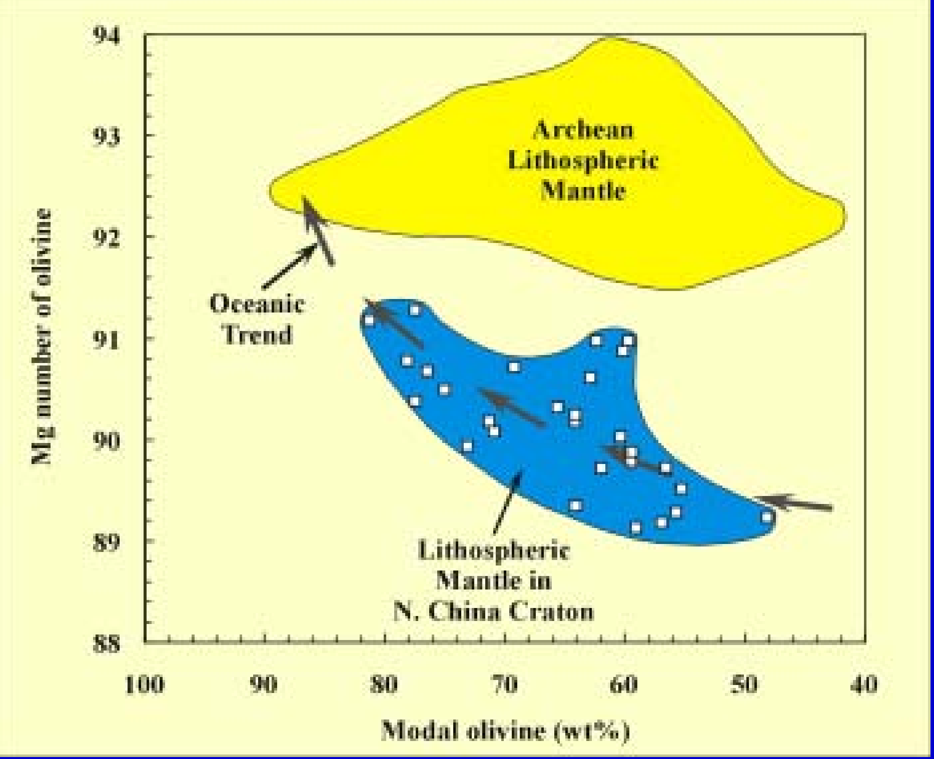
(Griffin et al., 1998)

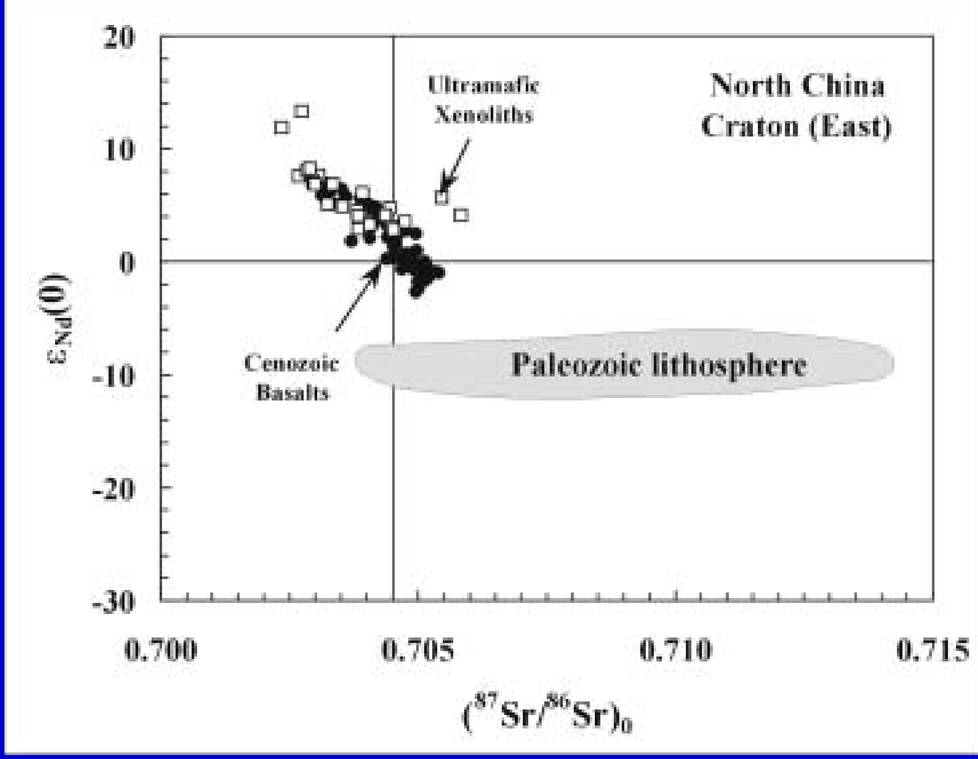
Xu YG, 2001. Phy. Chem. Earth (A), 26: 747-757.



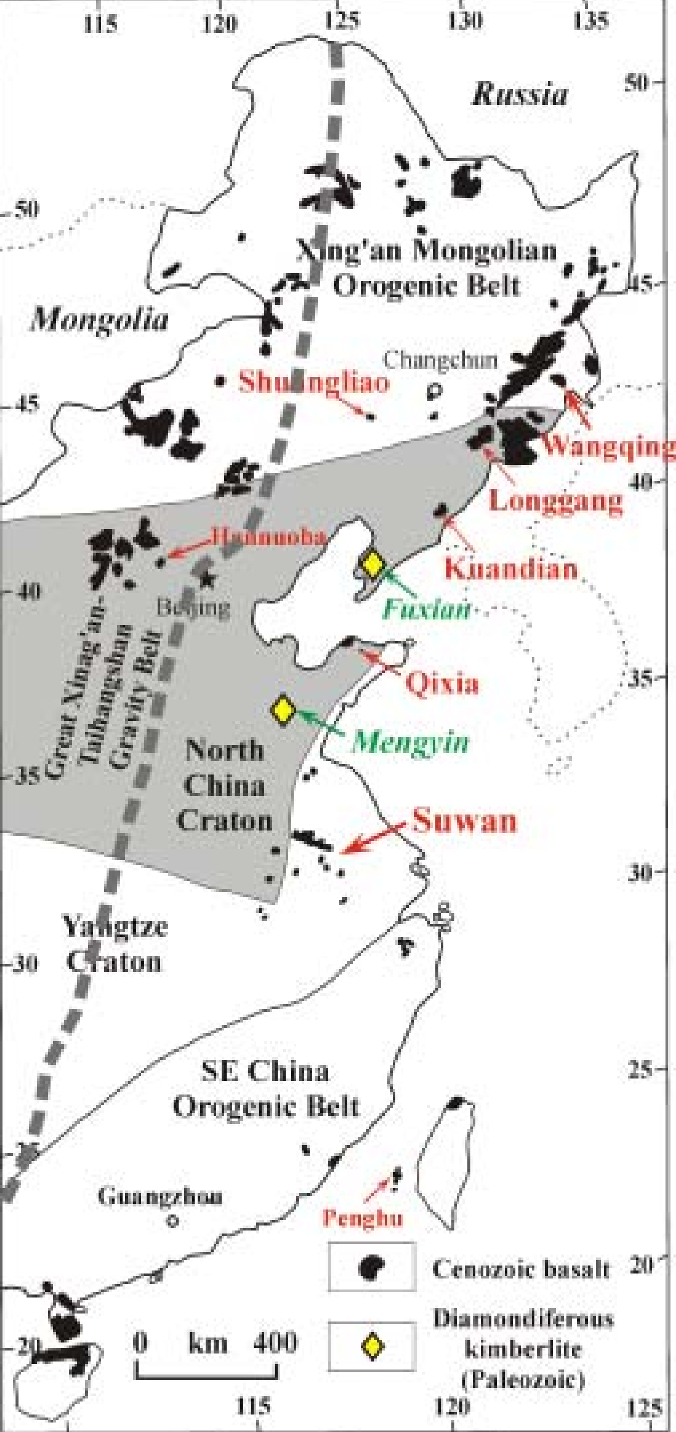
One question needed to be answered:

The present SCLM is Juvenile or the residue after thinning?





Petrography, mineral chemistry, and Sr-Nd isotopes indicated that the present SCLM is much different from that in the Paleozoic, indicating the whole-scale removal of the ancient SCLM during the Phanerozoic. However, it could be argued that the Paleozoic SCLM is stratified with enriched in lower and depleted in upper parts.



Os data of mantle xenoliths in eastern China

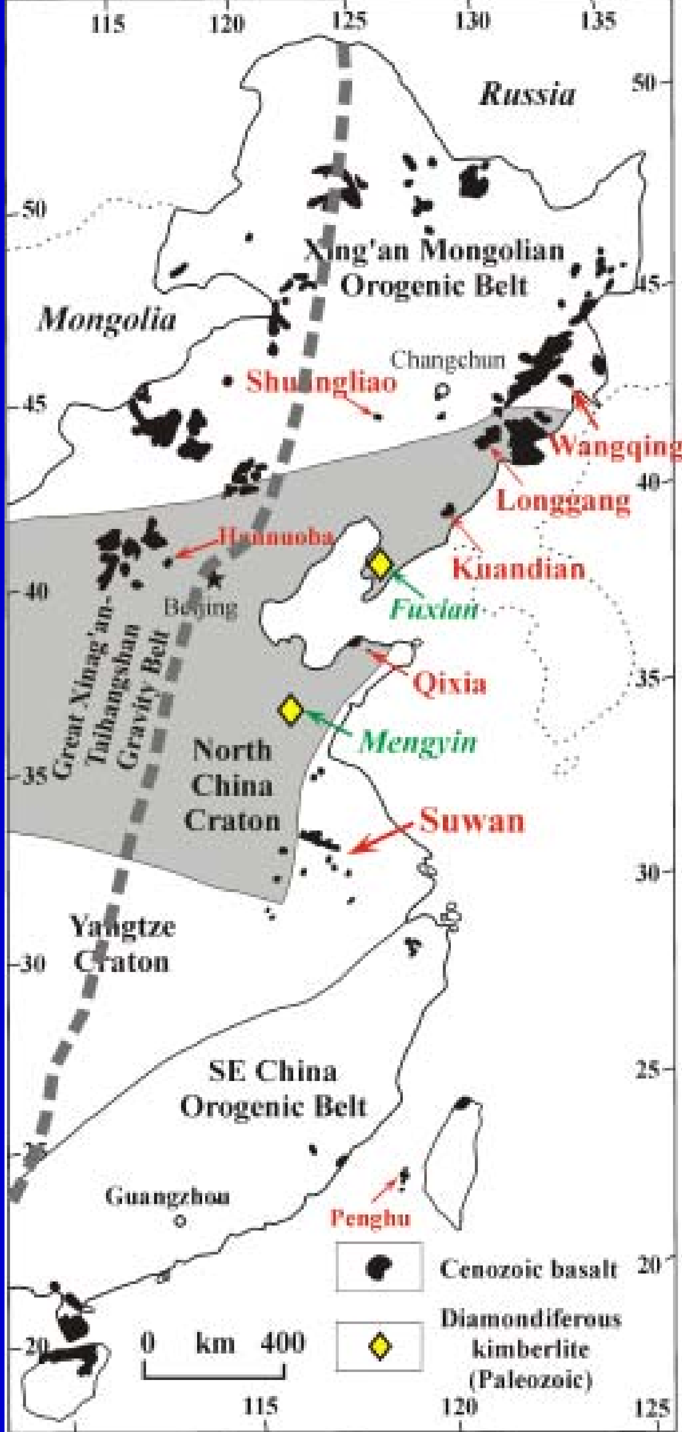
(1) Xing'an-Mongolian Orogenic Belt:
Wangqing, Shuangliao

(2) North China Craton
Hannuoba, Longgang, Kuandian, Qixia

(3) Yangtze Craton
Suwan

(4) SE China Belt
Penghu

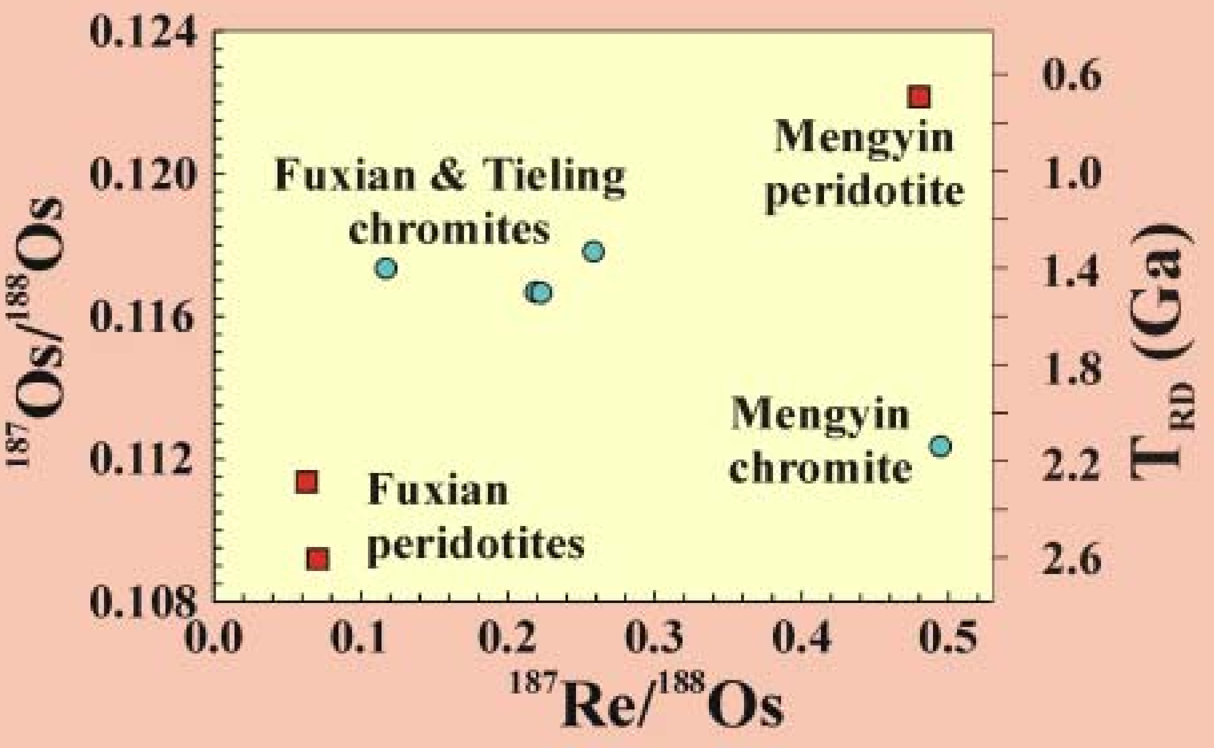
Zhi, et al., 2001. Sci. China (D), 44: 1110-1118.
Zhi and Qin, 2004. Acta Petrol. Sinica, 20: 989-998.
Gao et al., 2002. EPSL, 198, 307-322.
Wu et al., 2003. Chem. Geol., 196: 107-129.
Wu et al., 2005. In preparation.



Paleozoic SCLM: Os data

Archean + Proterozoic(?)

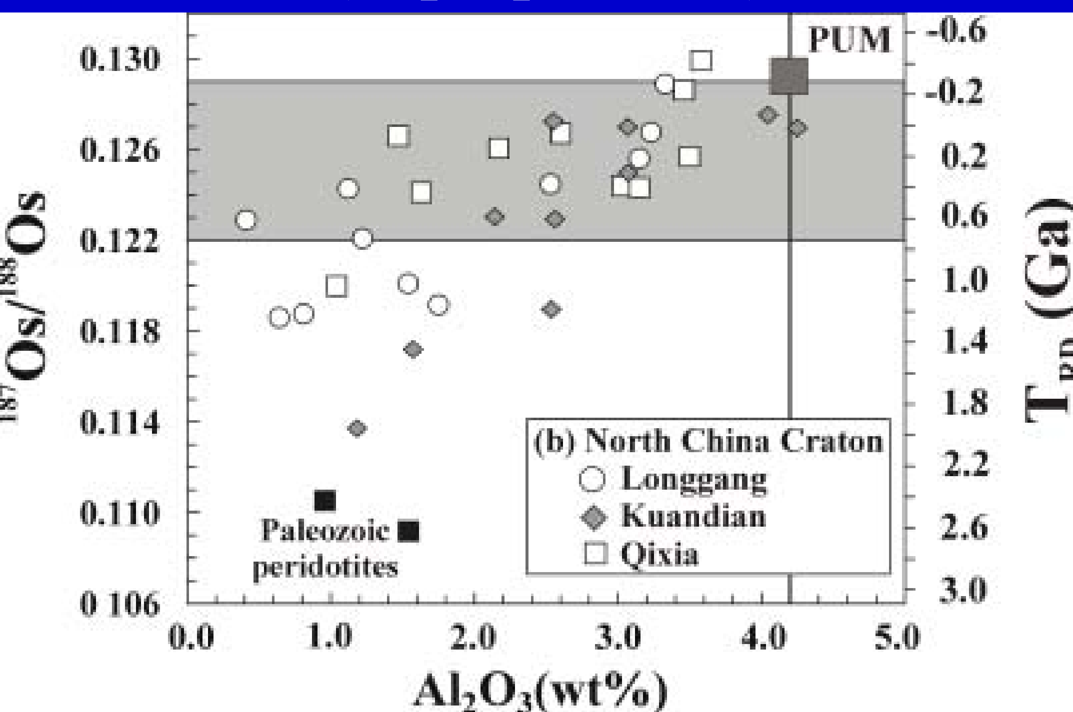
Peridotite xenoliths (Gao et al., 2002)
Chromite in kimberlite (Wu, unpublished)

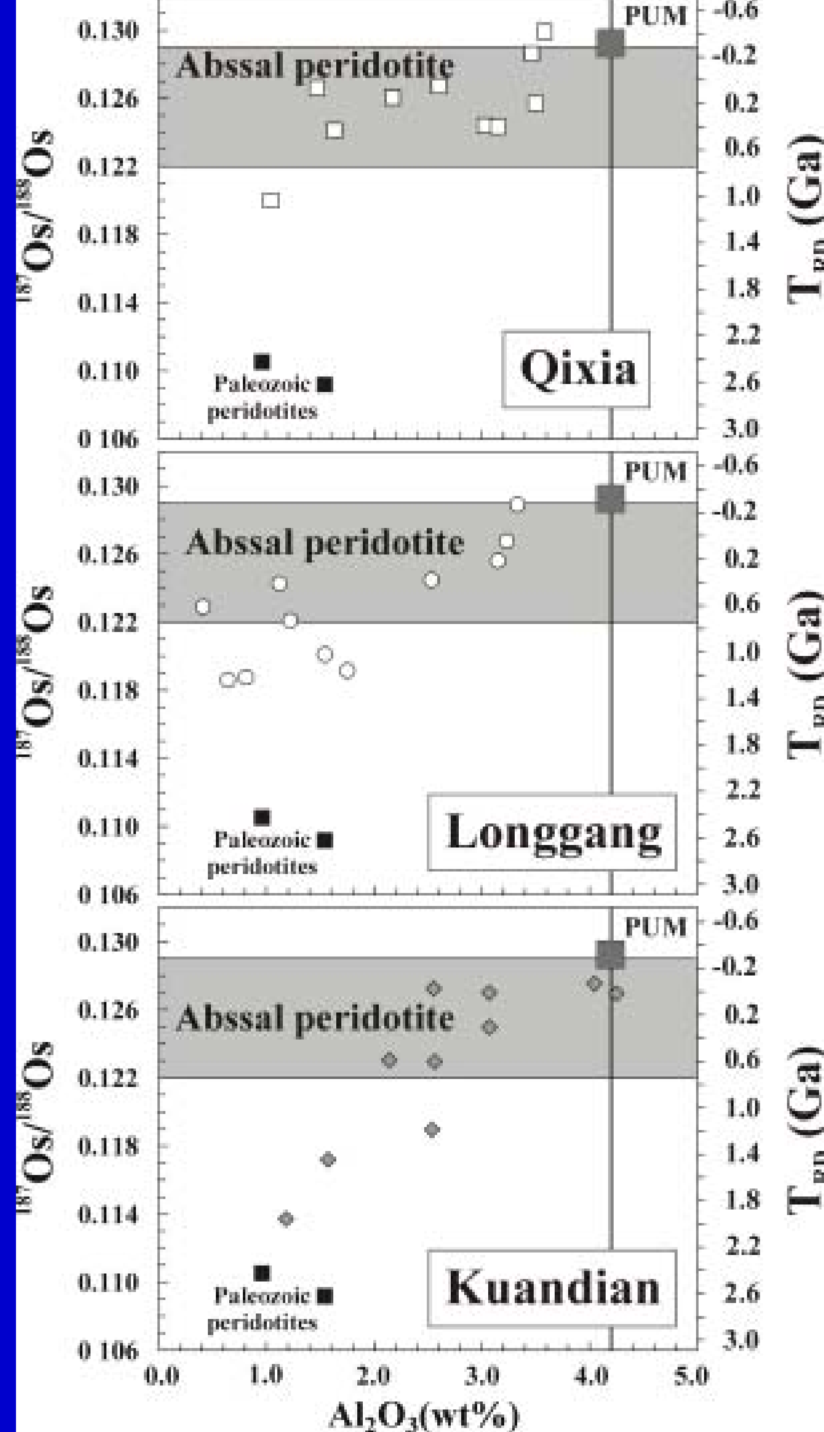


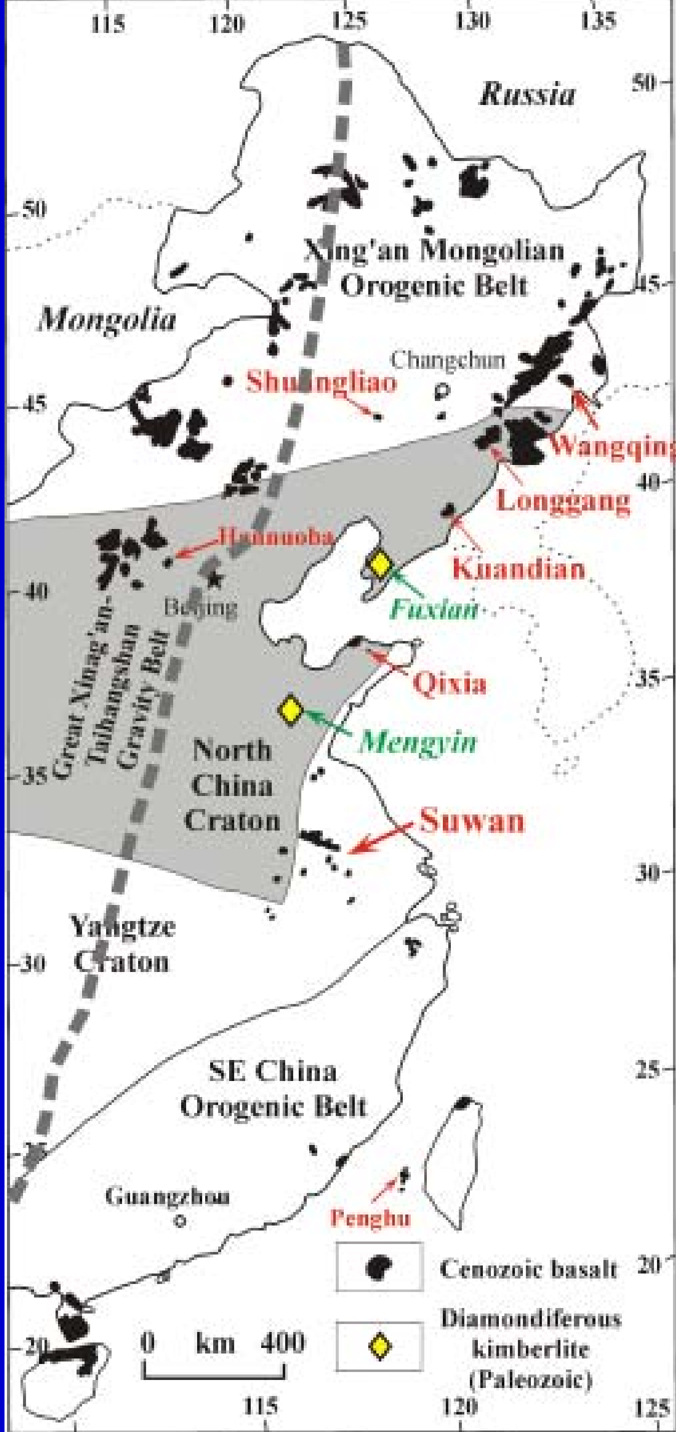
Cenozoic SCLM

No Archean at all!

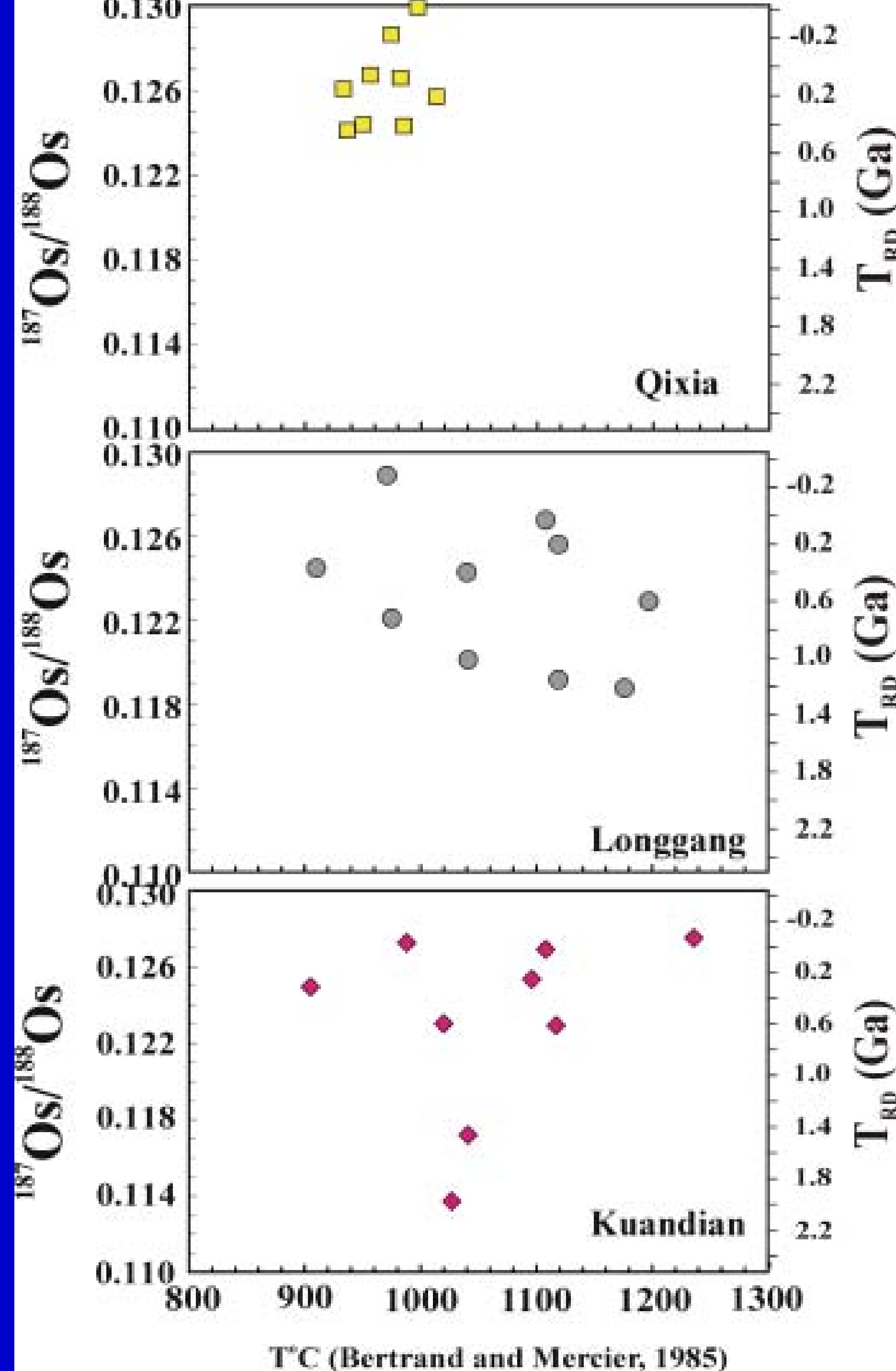
Qixia (Gao et al., 2002)
Longgang (Wu et al., 2003)
Kuandian (in preparation)

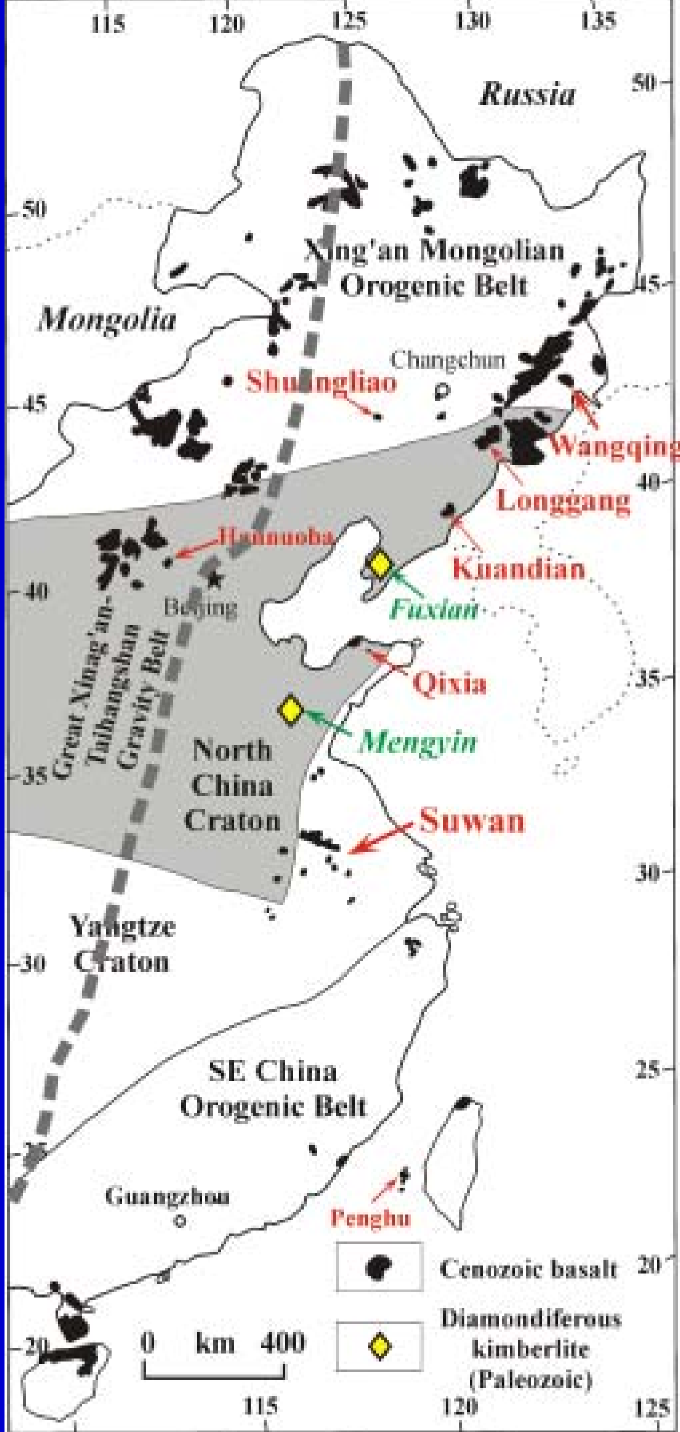




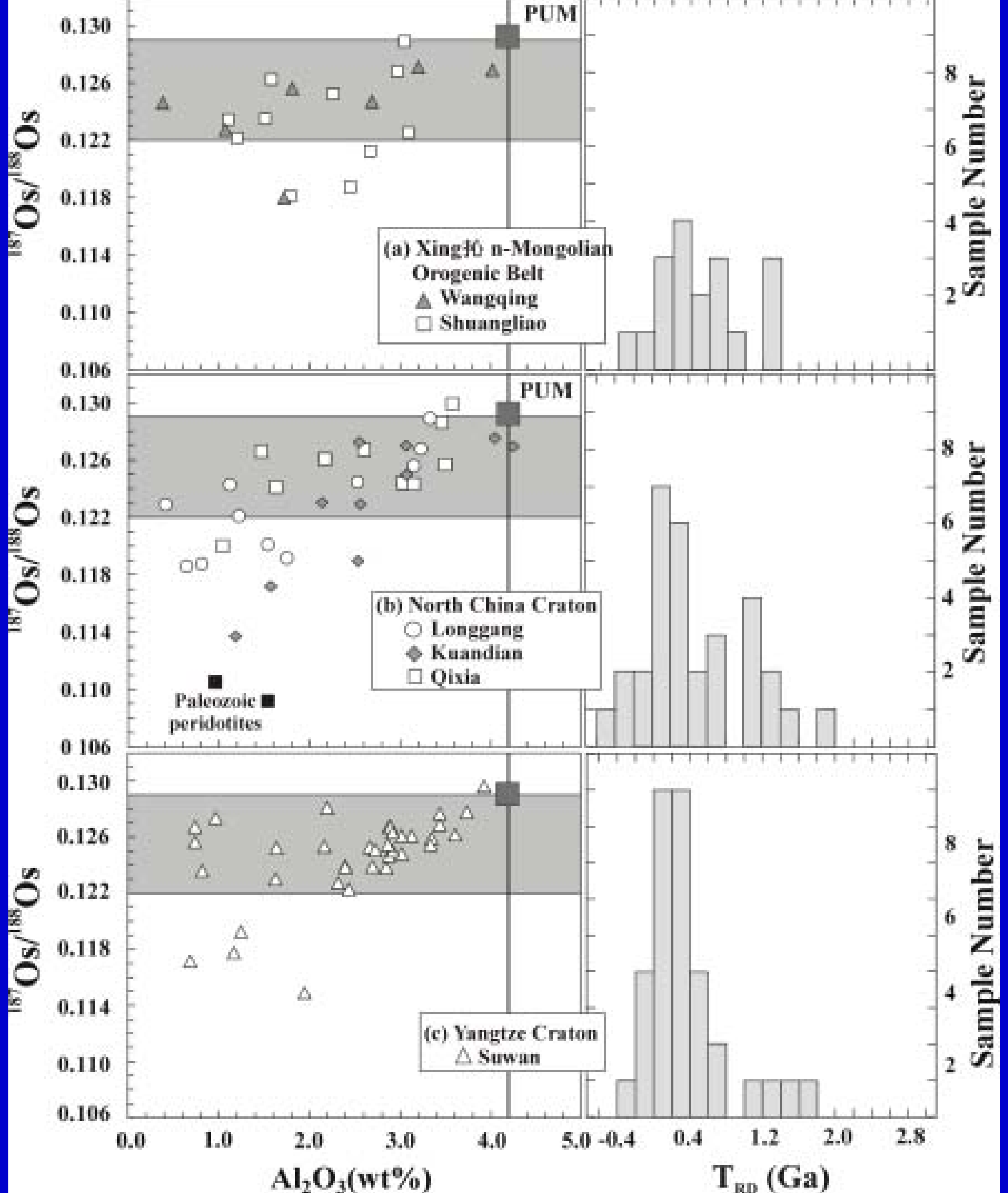


No stratification for the SCLM!





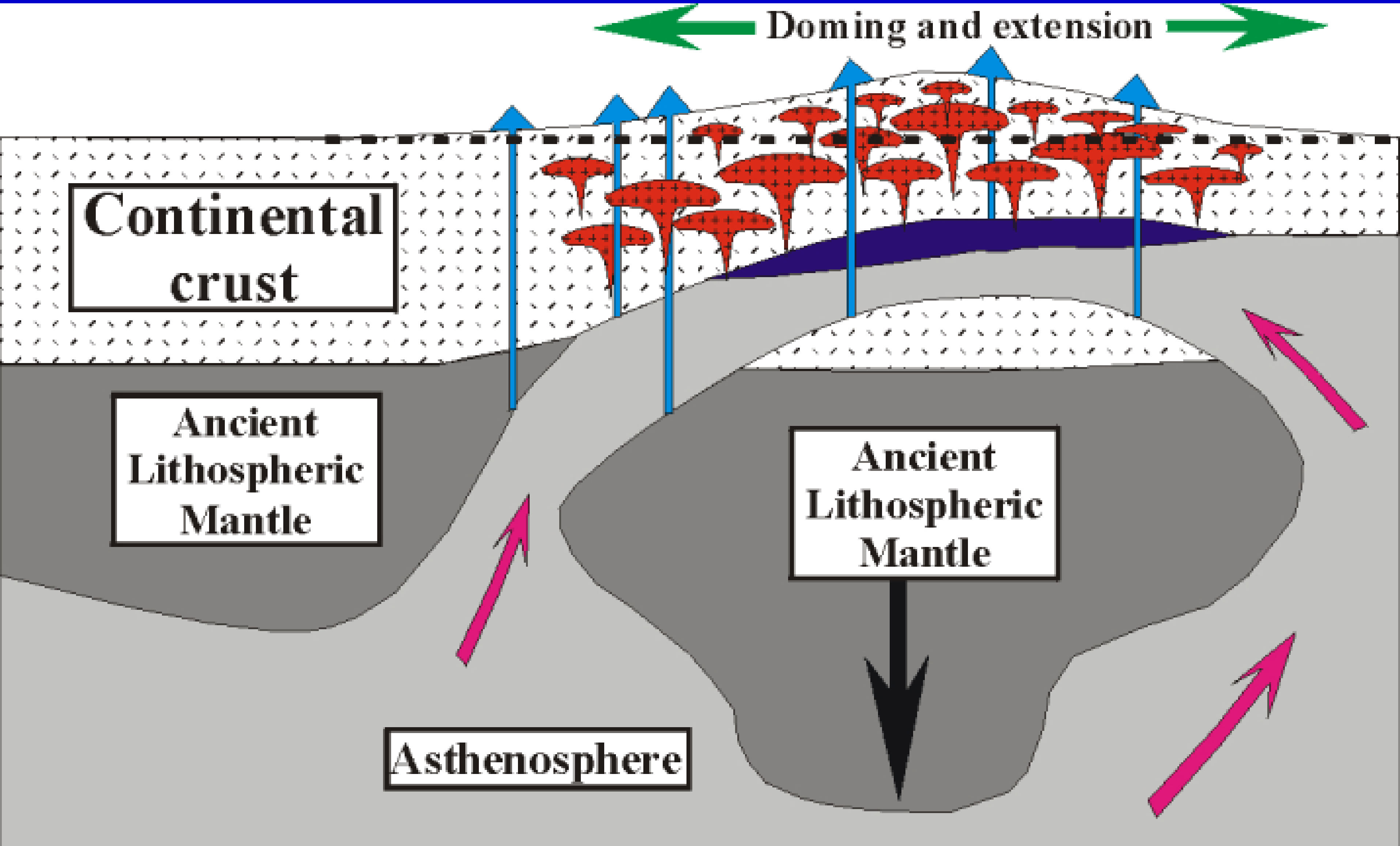
Russia
Mongolia
Xing'an Mongolian Orogenic Belt
Changchun
Shuangliao
Wangqing
Longgang
Hannuoba
Beijing
Kuandian
Fuxian
Qixia
Mengyin
Great Xinag'an-Taihangshan Gravity Belt
North China Craton
Suwan
Yangtze Craton
SE China Orogenic Belt
Guangzhou
Penghu
Cenozoic basalt
Diamondiferous kimberlite (Paleozoic)
0 km 400
115
120
125
130
135
50
45
40
35
30
25
20



PUM
(a) Xing拓 n-Mongolian Orogenic Belt
Wangqing
Shuangliao
(b) North China Craton
Longgang
Kuandian
Qixia
Paleozoic peridotites
(c) Yangtze Craton
Suwan
$^{187}Os/^{188}Os$
0.130
0.126
0.122
0.118
0.114
0.110
0.106
0 106
Sample Number
Al_2O_3(wt%)
0.0 1.0 2.0 3.0 4.0 5.0
T_{RD} (Ga)
-0.4 0.4 1.2 2.0 2.8

In terms of Os isotope, Cenozoic SCLM beneath the eastern NCC is mainly juvenile, with some of Proterozoic, but it is not stratified. Therefore, it is suggested that the present SCLM is not the ancient residue after thinning.

Lithospheric thinning of the NCC



多谢指正！