Measuring the ages of granites: the challenge to get it right

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To measure the ages of igneous rocks by isotope geochronology is, in principle, a relatively simple procedure. There is a variety of dating techniques to choose from (e.g. K–Ar, Ar–Ar, Rb–Sr, U–Pb, Sm–Nd) and, with a few exceptions, the technicalities of each method are well understood. This point has been reached only by considerable trial and error, however, particularly when it comes to dating granites.

In the very simplest case, accurate dating of an igneous rock requires two basic conditions to be satisfied. When the rock crystallised, it must have incorporated the radioactive isotope of choice, but none of its stable daughter product. After crystallisation, the rock must have remained a closed system—no daughter or parent isotopes can have been added to, or lost from, the rock other than by in situ radioactive decay. Rarely are these criteria met, although the K–Ar system in erupted basalt magmas is one such example. Most igneous rocks, including granites, incorporate significant amounts of all the decay products of interest, even Ar, at the time of crystallisation. One solution is to analyse, not the granite as a whole, but selected minerals that concentrate the radioactive element of choice yet exclude its decay product. Micas and hornblende, for example, are enriched in K but contain trivial Ar, micas are strongly enriched in Rb relative to Sr, and some trace minerals such as zircon and monazite are enriched in U but exclude Pb.

Much of the early dating work on granites was done using mineral K–Ar and Rb–Sr. The requisite micas and hornblende were relatively abundant and easy to separate, the enrichments in K and Rb were large, and the procedures for extracting and analysing the elements of interest were not particularly difficult. There was the minor complication that some micas contain significant amounts of initial Sr, but its isotopic composition could be measured on Sr-rich, Rb-poor minerals and a correction made. A refinement of the Rb–Sr technique was to measure the composition of a variety of minerals with different initial Rb/Sr ratios, and commonly also the whole rock. If the isotopic composition of the initial Sr was the same for all, which it should be in an isotopically homogeneous magma, then a plot of mineral Sr isotopic composition versus Rb/Sr defined an isochron, the slope of which gave the age of the rock. Ages were measured with analytical precisions of about 0.25%.

The widespread use of K–Ar and Rb–Sr mineral dating provided the first direct measurements of granite ages on a regional scale, and thereby the first direct measurements of the extent and duration of those magmatic events. As the data base increased, however, inconsistencies emerged. Occasionally ages were higher than expected, indicating the presence of excess argon. More commonly ages were lower than expected, reflecting a radiogenic Ar and Sr deficiency. Biotite only retains radiogenic Sr and Ar quantitatively below about 350 ˚C. Muscovite and hornblende have closure temperatures of about 500 ˚C. Only if granites cooled quickly and remained unmetamorphosed were K–Ar and Rb–Sr ages an accurate estimate of the emplacement ages. Where magmatic provinces had cooled slowly or been metamorphosed, these ages simply recorded the last time that the various minerals had cooled below their closure temperatures.

Rb–Sr analysts attempted to solve this problem by measuring ages using only whole rocks. Although some radiogenic Sr might be lost from individual minerals, it was expected to remain within the rock, so the isotopic age of the granite would be preserved. Whole-rock dating relies on granitic magmas being isotopically, but not chemically, homogeneous. Rb–Sr analyses of several rocks from a single intrusion are therefore expected to define an isochron, the slope indicating the granite age and the intercept its initial Sr isotopic composition. In practice the whole-rock dating method has major weaknesses. First, most granites are chemically relatively homogeneous, with much lower Rb/Sr than minerals such as micas. To obtain rocks with enough range in Rb/Sr to define an isochron precisely can be very difficult, and it is not necessarily valid to extend the range by sampling enclaves and aplites. Secondly, the Sr isotopic composition of a granitic magma is rarely homogeneous. If the heterogeneity is random, then the whole-rock analyses scatter about the isochron, making the age determination imprecise, even if many rocks are analysed. More importantly, if the initial Sr isotopic variation is not random, but correlated with Rb/Sr, then the age of the granite can be grossly overestimated. Constructing isochrons from analyses of rocks that are not cogenetic can cause similar errors.

K–Ar analysts tackled the problems of excess Ar and Ar loss by developing the ^{40}Ar–^{39}Ar technique, whereby neutron irradiation is used to convert some of the ^{39}K in a mineral into ^{39}Ar. The method assumes that in cases of partial radiogenic Ar loss, some domains in some mineral grains remain unaffected, and that excess Ar has a different distribution in mineral grains from the Ar produced by *in situ* ^{40}K decay. When the irradiated mineral separate is step heated to release its Ar in small increments, the most loosely held Ar is released first and the most tightly held Ar released last. ^{39}Ar being a proxy for ^{40}K, the ^{40}Ar/^{39}Ar of each gas fraction gives its K–Ar age. Excess Ar is identified by its high ^{40}Ar/^{39}Ar, Ar from domains of Ar loss by its low ^{40}Ar/^{39}Ar. Domains unaffected by either process yield the same ^{40}Ar/^{39}Ar (hence same age) over several temperature steps. The ^{40}Ar–^{39}Ar technique has been applied very successfully to granites, although crystallographic effects on Ar release sometimes reduce the precision of ages measured on biotite. The technique is still limited, however, by the relatively low closure temperatures of the minerals analysed.

Slow cooling and metamorphism are lesser issues for U–Pb dating. Zircon, the mineral most commonly used for U–Pb dating of granites, has a closure temperature of over 900 ˚C, comparable to the temperatures of high-temperature granitic magmas. Even so, zircon was slow to be widely used for geochronology because of the technical difficulties involved. To obtain enough trace zircon for analysis required tens to hundreds of kilograms of rock, the chemical procedures for extracting and purifying U and Pb were complex, and the isotopic analysis of Pb was very difficult. Following development of improved chemical and mass spectrometric techniques, however (high-pressure bombs, ultra-pure reagents, ion-exchange chemistry, silica gel), zircon U–Pb quickly became the method of choice for dating granite, particularly in terranes with complex thermal histories. The technique continues to be developed, wet chemical isotopic analyses of single 10 µg zircon grains now being commonplace, producing age determinations with analytical precisions of better than 0.1%. The accuracy that can be achieved is now limited principally by the uncertainties in the U decay constants.

Zircon geochronology also has its limitations, however. Many granitic magmas, particularly magmas produced by low-temperature partial melting of predominantly crustal rocks, are zircon saturated. Zircon is an extremely robust mineral, both physically and chemically, so zircon from the source rocks of granites, and also potentially from wall rocks, becomes entrained in granitic magmas and preserved in the consequent granitic rocks. This inherited older zircon acts as nuclei for the new zircon precipitated during magma genesis. The radiogenic Pb in the inherited nucleus is preserved, so U–Pb dating of even single zircon crystals can yield, not the age of the granite, but the meaningless averaged ‘age’ of a mixture. Inherited zircon is particularly common in the Palaeozoic granites of eastern Australia, making accurate zircon age measurements by wet chemistry extremely difficult.

Melt-precipitated zircon in inheritance-rich granites is best dated by *in situ* microsampling. This can presently be done by ion microprobe (SIMS) or laser ICP-MS. In both cases the zircon samples are prepared as grain mounts which are polished to section the grains and expose their growth zones. For SIMS analysis, a 10–30 µm diameter beam of oxygen ions is focused onto the zircon, sputtering secondary ions that are analysed in a double-focusing mass spectrometer. Each analysis takes about 15 minutes, the ion beam penetrating about 2 µm into the grain. For laser ICP-MS analysis, a 10–100 µm diameter laser beam is used to ablate particles that are dissociated and ionised in a plasma then analysed in a rapid-switching magnetic sector or quadrupole mass spectrometer. Each analysis takes about 2 minutes, the laser beam penetrating 10–100 µm into the grain. The precision of individual Pb/U analyses by the two techniques is similar, normally 0.5–4%, depending upon U content. Much higher precision on the final age determination is achieved when multiple analyses are pooled. Precision must not be confused with accuracy, however. The accuracy of both techniques is limited by the need to calibrate the Pb/U measurements against either zircon (SIMS, ICP-MS) or solutions (ICP-MS) of known composition. Calibrations against zircon in both cases are limited by the micron-scale heterogeneity of available natural standards. The best accuracy achieved by both techniques is currently about 1%, although some issues of inaccuracy up to 5% still remain to be resolved.

Microsampling makes it possible to date melt-precipitated zircon free from the effects of older inherited zircon. It also makes it possible to date the inheritance, and thereby to obtain direct information on the age and relative abundance of the zircon components incorporated in the granite magma. These inherited ages appear to be preserved unaffected by the magmatism, and provide valuable 'fingerprints' that help to identify the likely sources of the granites and even the possible provenance of those sources. Microsampling is equally applicable to dating other U-rich trace minerals, for example titanite and monazite, but as with zircon, in the absence of inheritance or severe isotopic disturbance, the best precision and accuracy is still obtained by wet chemical techniques.

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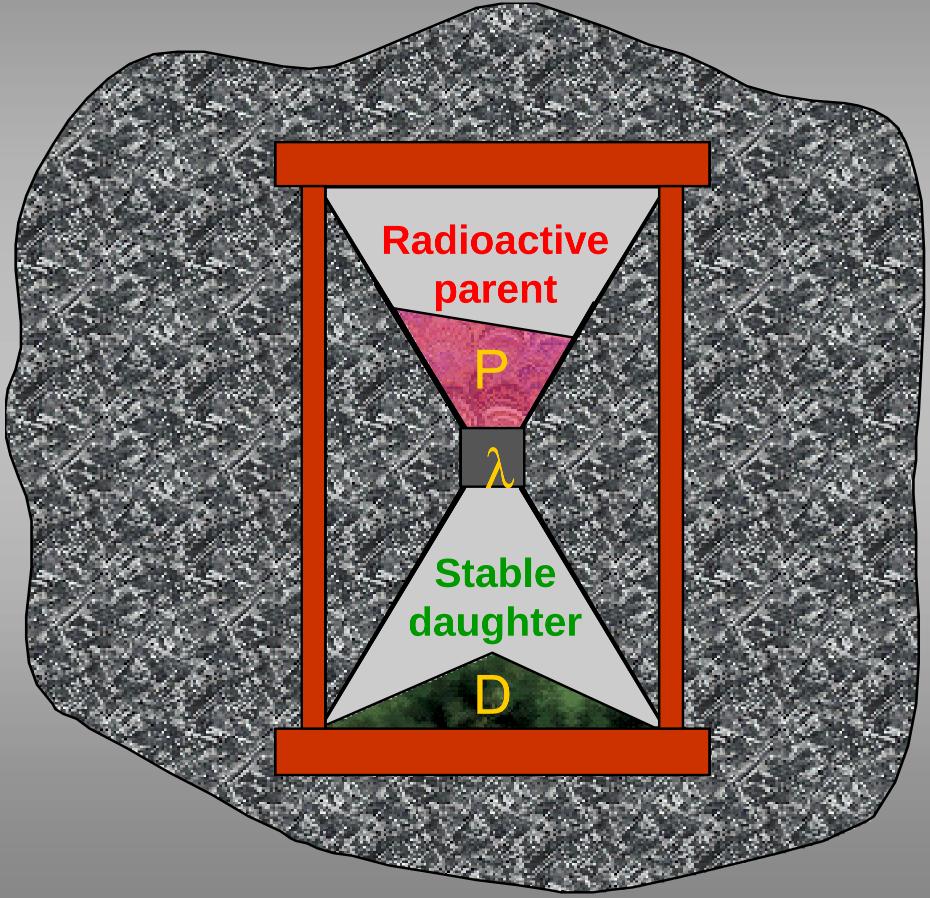
Radioisotope geochronology in concept

$$t = \frac{\ln(D/P + 1)}{\lambda}$$



Common geochronometers

Long half lives on a geological time scale

		Half life
$^{40}\mathrm{K} \longrightarrow$	$^{40}\mathrm{Ar}$ (and $^{40}\mathrm{Ca}$)	1.25 Ga
$^{87}\mathrm{Rb} \longrightarrow$	$^{87}\mathrm{Sr}$	48.8 Ga
$^{238}\mathrm{U} \longrightarrow$	$^{206}\mathrm{Pb}$	4.47 Ga
$^{235}\mathrm{U} \longrightarrow$	$^{207}\mathrm{Pb}$	704 Ma
$^{147}\mathrm{Sm} \longrightarrow$	$^{143}\mathrm{Nd}$	106 Ga

K-Ar and Rb-Sr mineral ages

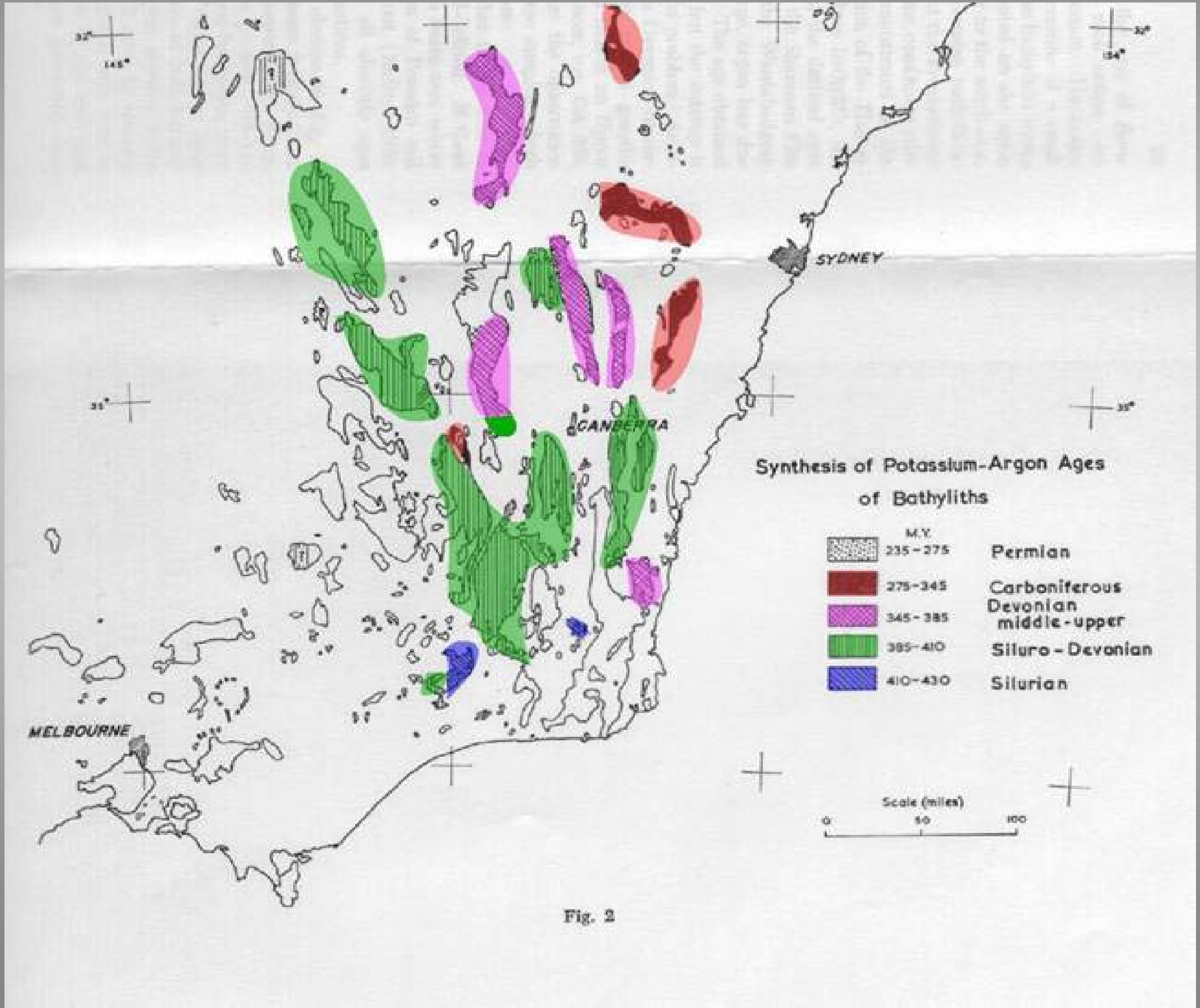
- High abundance host minerals (e.g micas)
- High radioactive parent content
- Low initial daughter content
- Reasonably simple sample preparation
- Reasonably simple analysis
- Good analytical precision (~0.5%)

Granite ages in eastern Australia

K-Ar

Evernden and Richards (1962)

~100 analyses

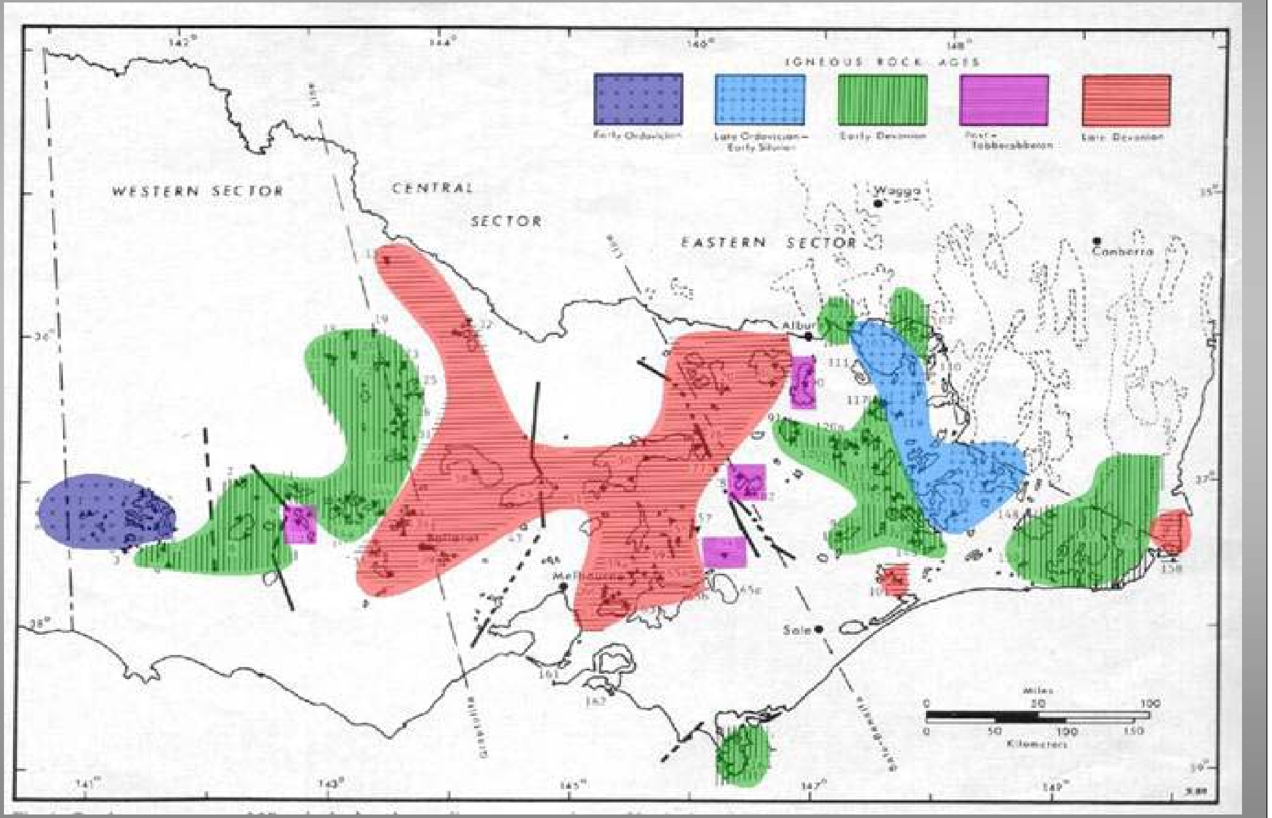


Granite ages in eastern Australia

K-Ar, Rb-Sr

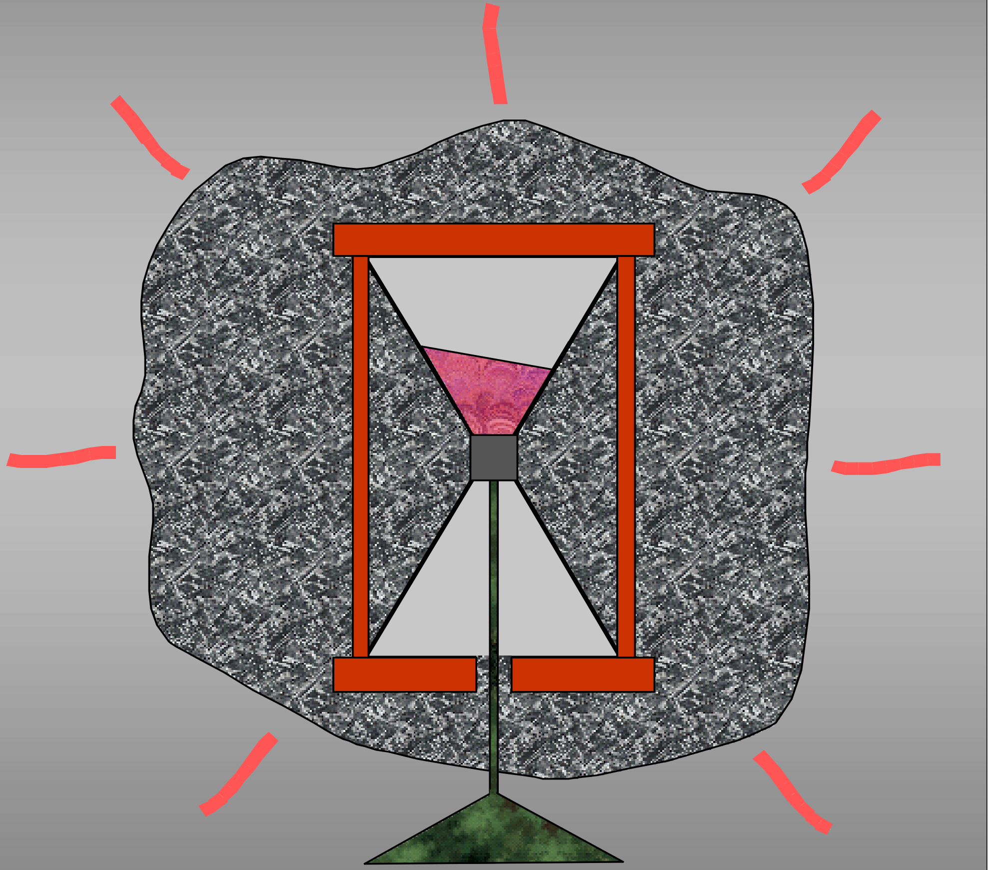
Richards and Singleton (1981)

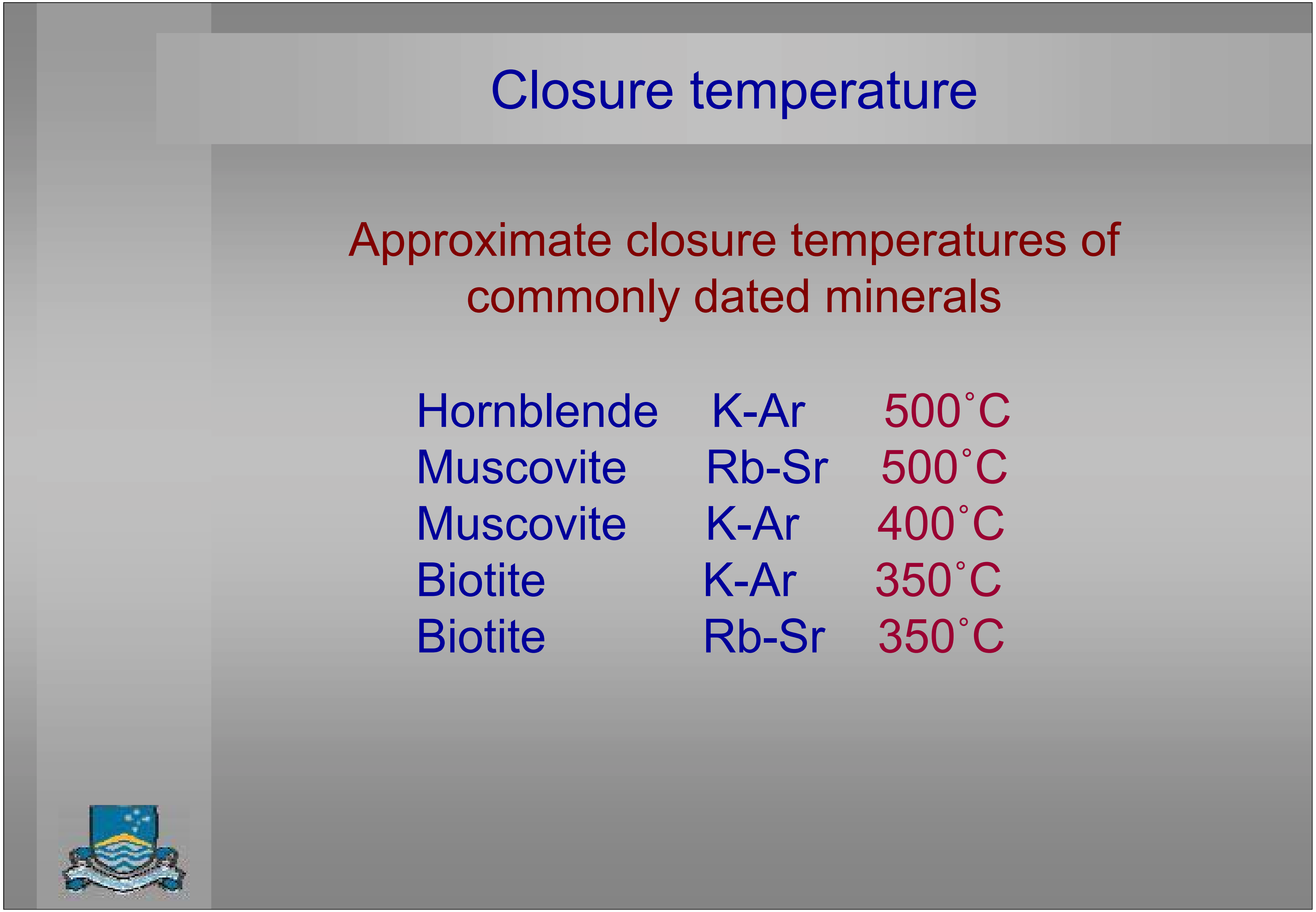
~160 analyses



Closure temperature

Minerals only retain radiogenic daughter products below their closure temperatures





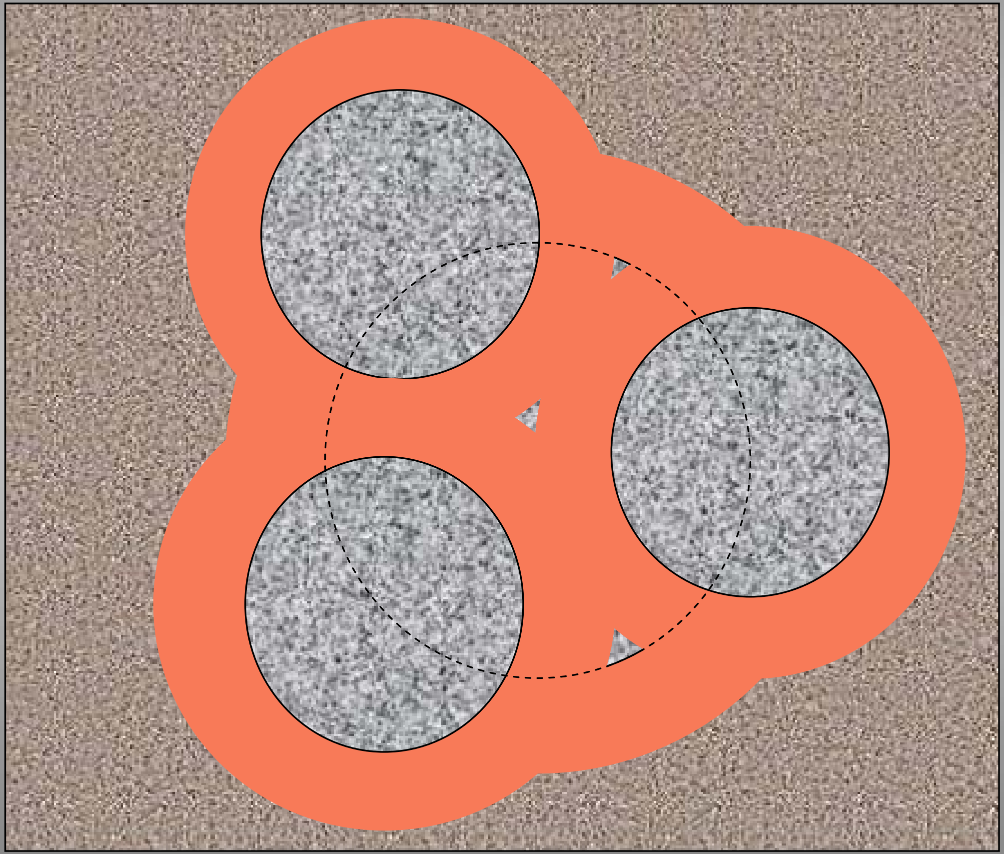
Closure temperature

Approximate closure temperatures of commonly dated minerals

Hornblende	K-Ar	500°C
Muscovite	Rb-Sr	500°C
Muscovite	K-Ar	400°C
Biotite	K-Ar	350°C
Biotite	Rb-Sr	350°C

Closure temperature

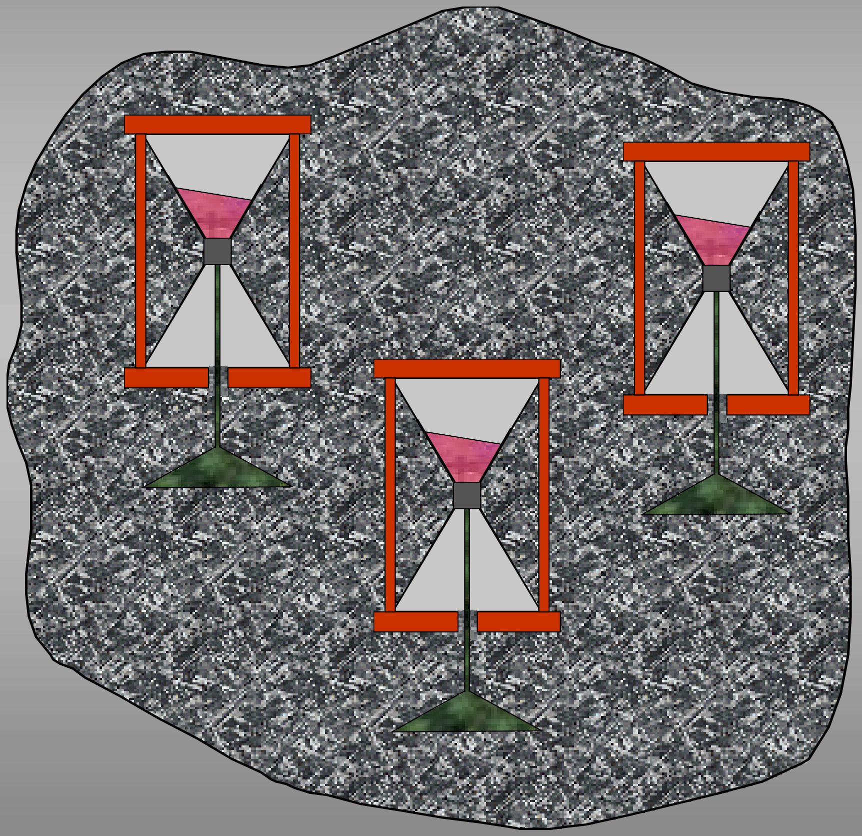
Younger plutons slow the cooling of older plutons



Rb-Sr whole rock analyses

Concept

Although individual minerals might ‘leak’, the whole rock remains closed

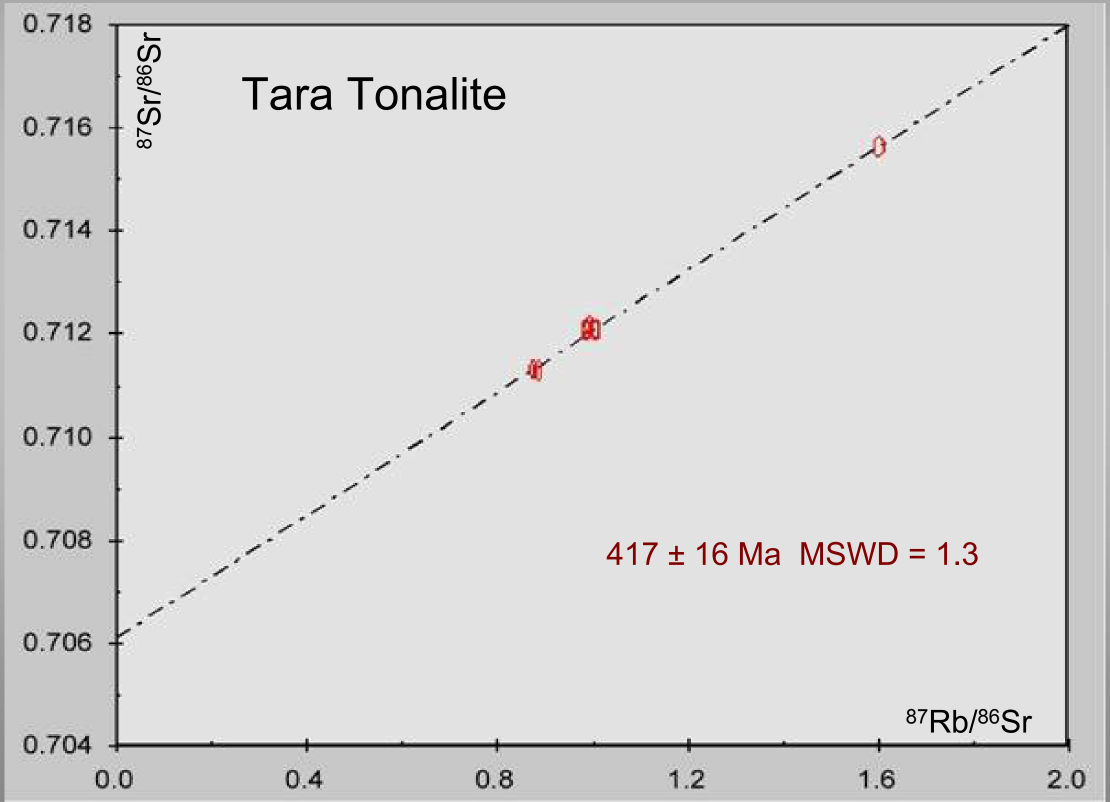


Eastern Australian granites

Rb-Sr whole rocks

Young I-type

Good isochron but little dispersion

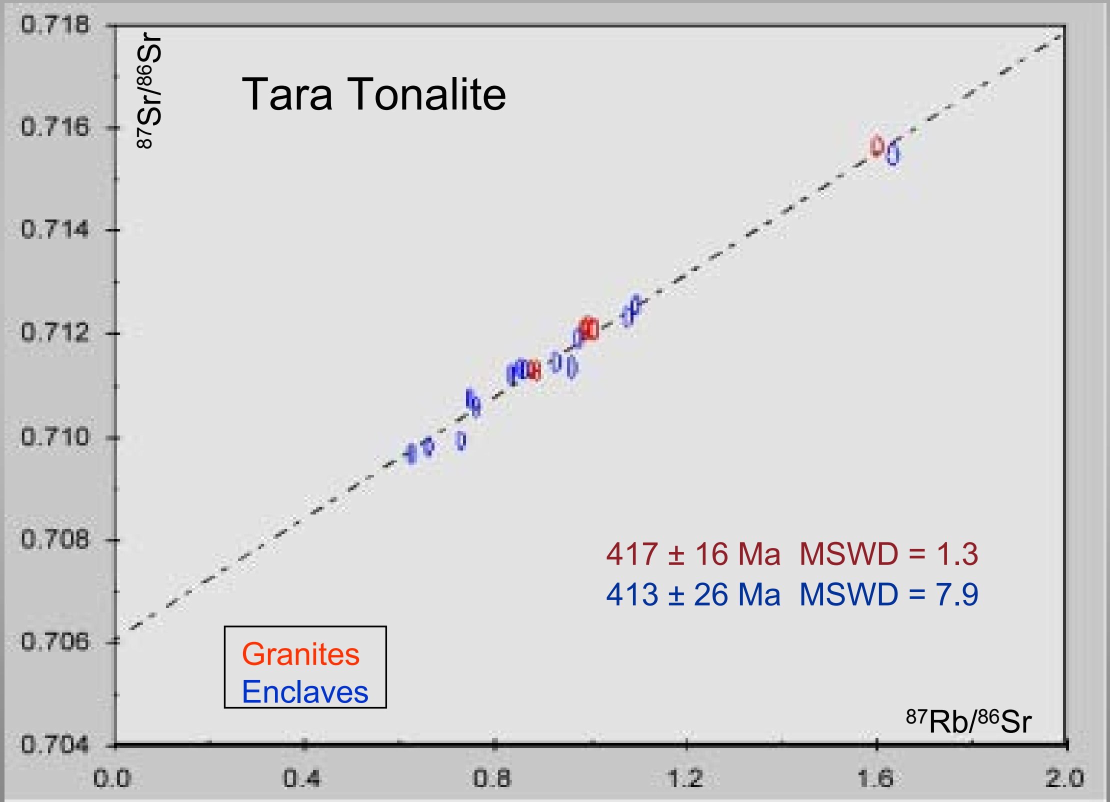


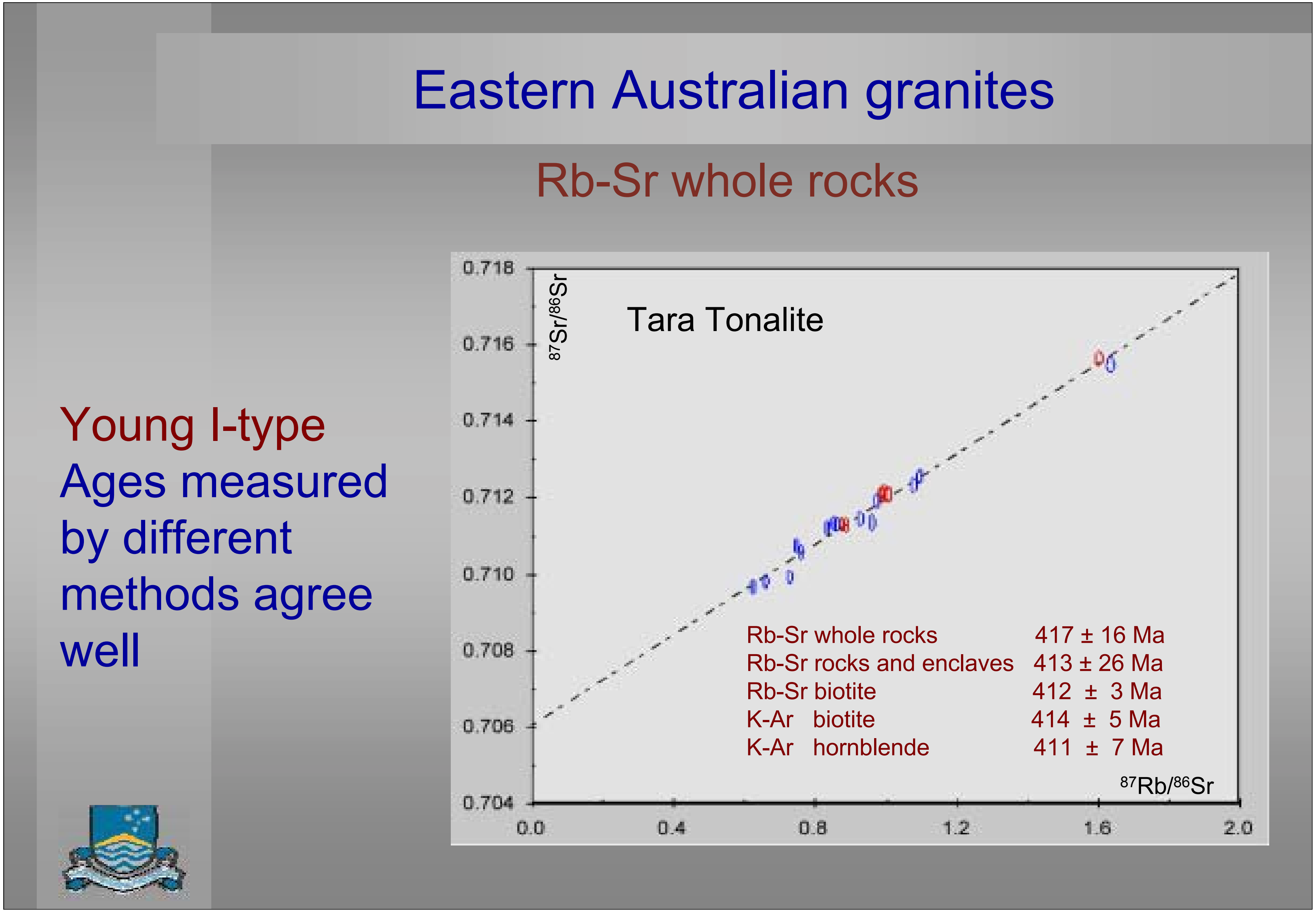
Eastern Australian granites

Rb-Sr whole rocks

Young I-type

Adding enclave analyses does not help





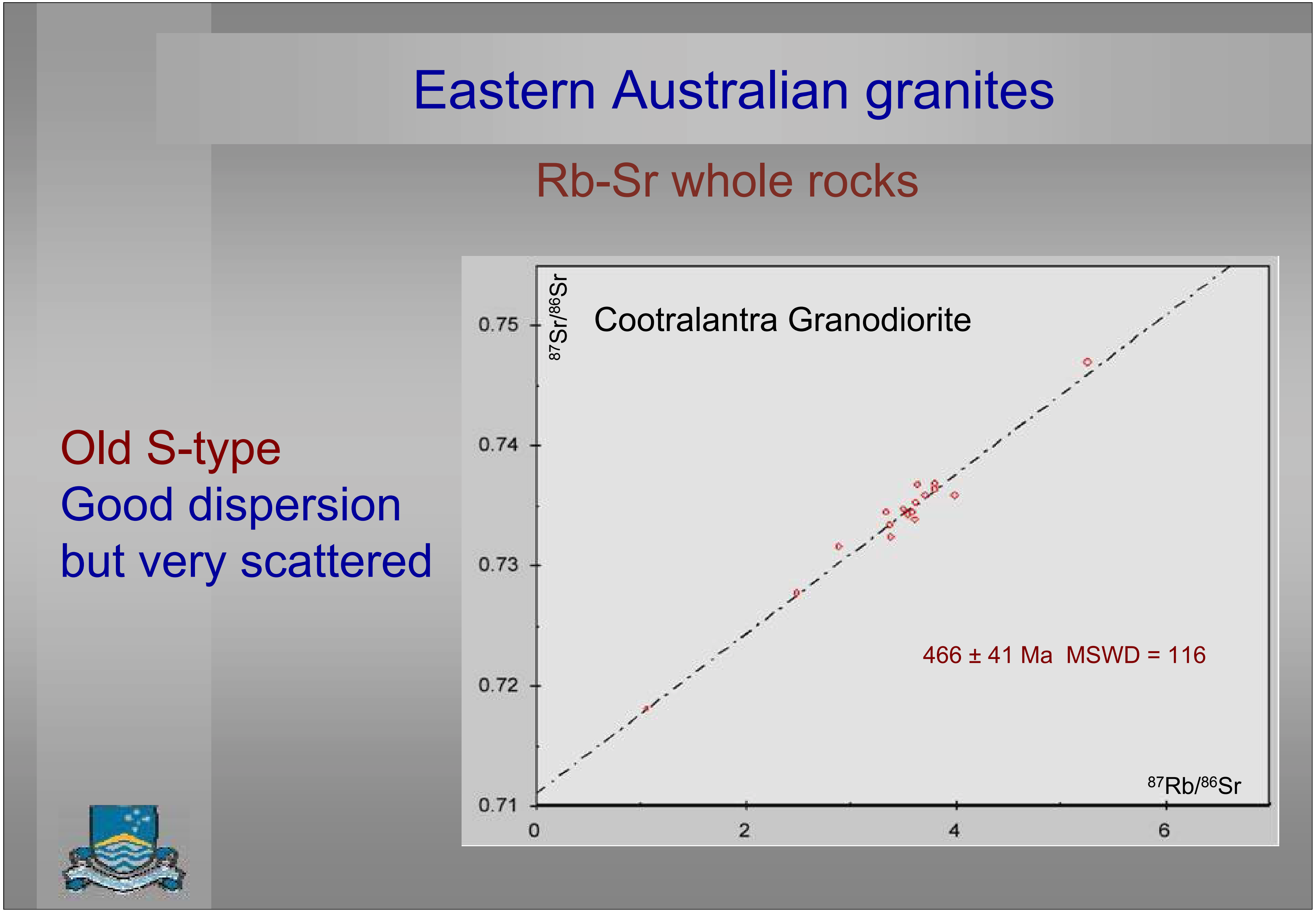
Eastern Australian granites

Rb-Sr whole rocks

Young I-type
Ages measured by different methods agree well

Tara Tonalite

Rb-Sr whole rocks	417 ± 16 Ma
Rb-Sr rocks and enclaves	413 ± 26 Ma
Rb-Sr biotite	412 ± 3 Ma
K-Ar biotite	414 ± 5 Ma
K-Ar hornblende	411 ± 7 Ma



Eastern Australian granites

Rb-Sr whole rocks

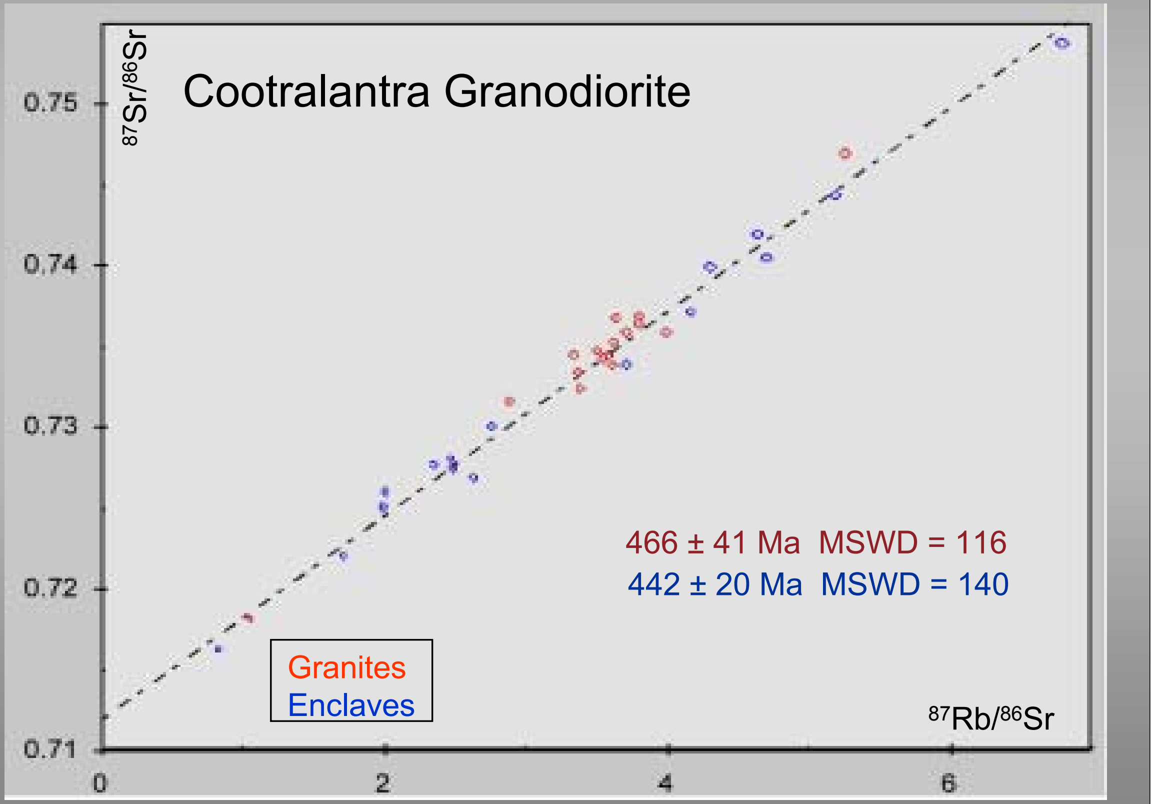
Old S-type
Good dispersion
but very scattered

Eastern Australian granites

Rb-Sr whole rocks

Old S-type

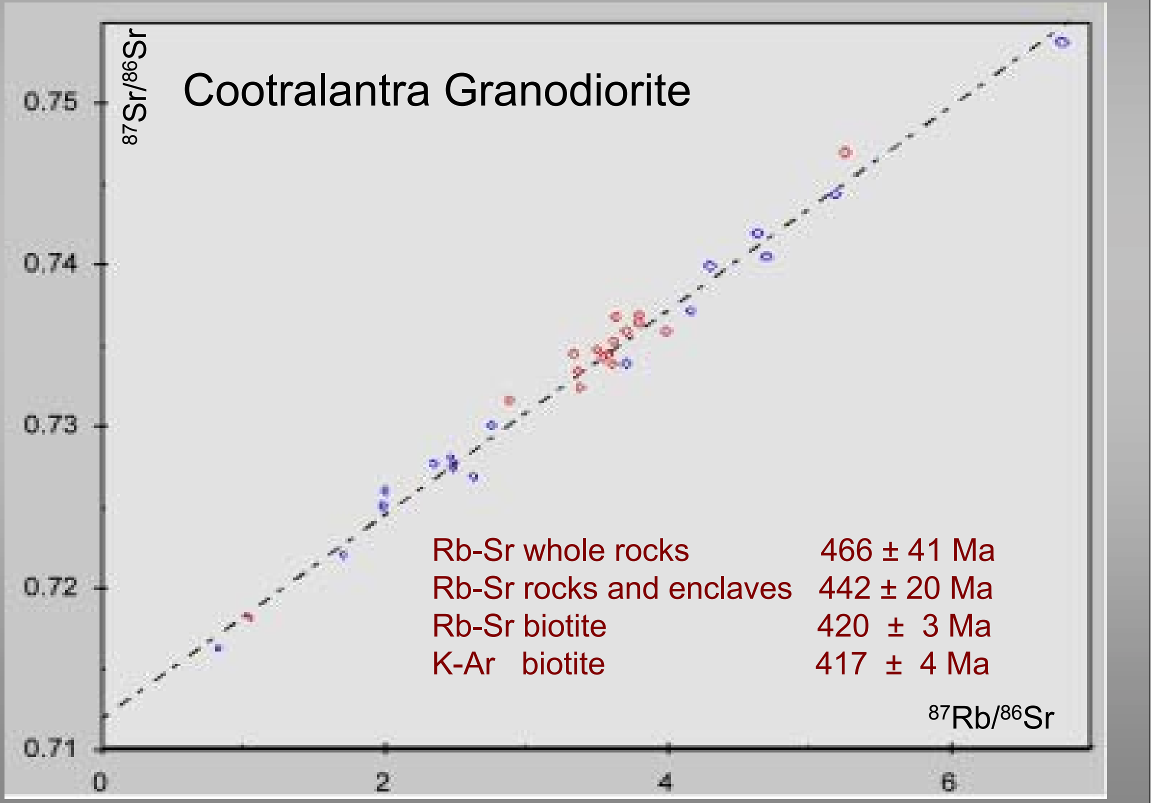
Enclaves increase scatter but improve precision



Eastern Australian granites

Rb-Sr whole rocks

Old S-type
Whole rocks
appear older than
minerals.
Which is ‘right’?



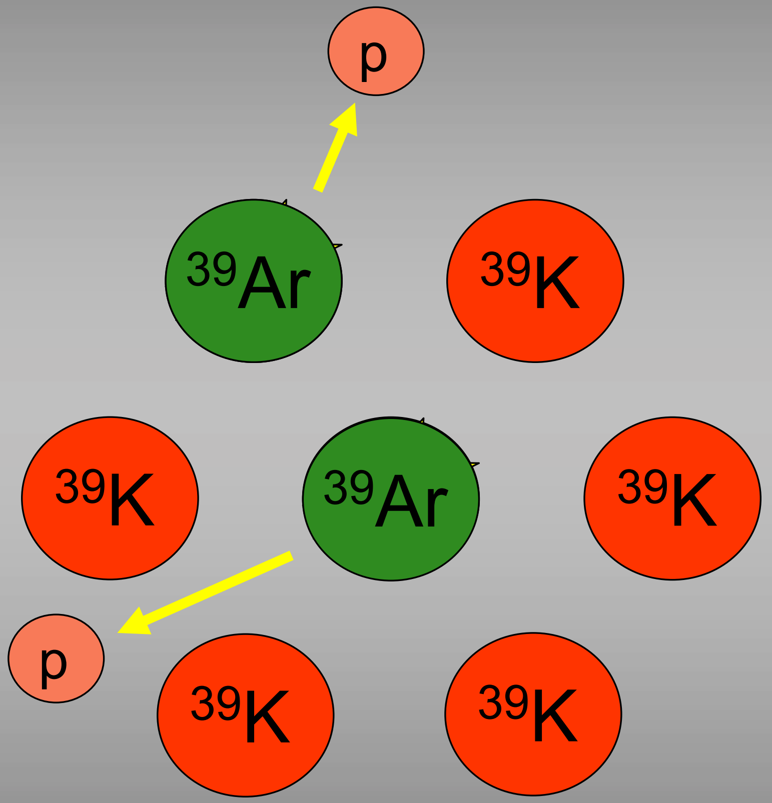
Rb-Sr whole rocks	466 ± 41 Ma
Rb-Sr rocks and enclaves	442 ± 20 Ma
Rb-Sr biotite	420 ± 3 Ma
K-Ar biotite	417 ± 4 Ma

^{40}Ar–^{39}Ar technique

^{39}K can be converted to ^{39}Ar by fast neutron irradiation.

A neutron is captured and a proton lost.

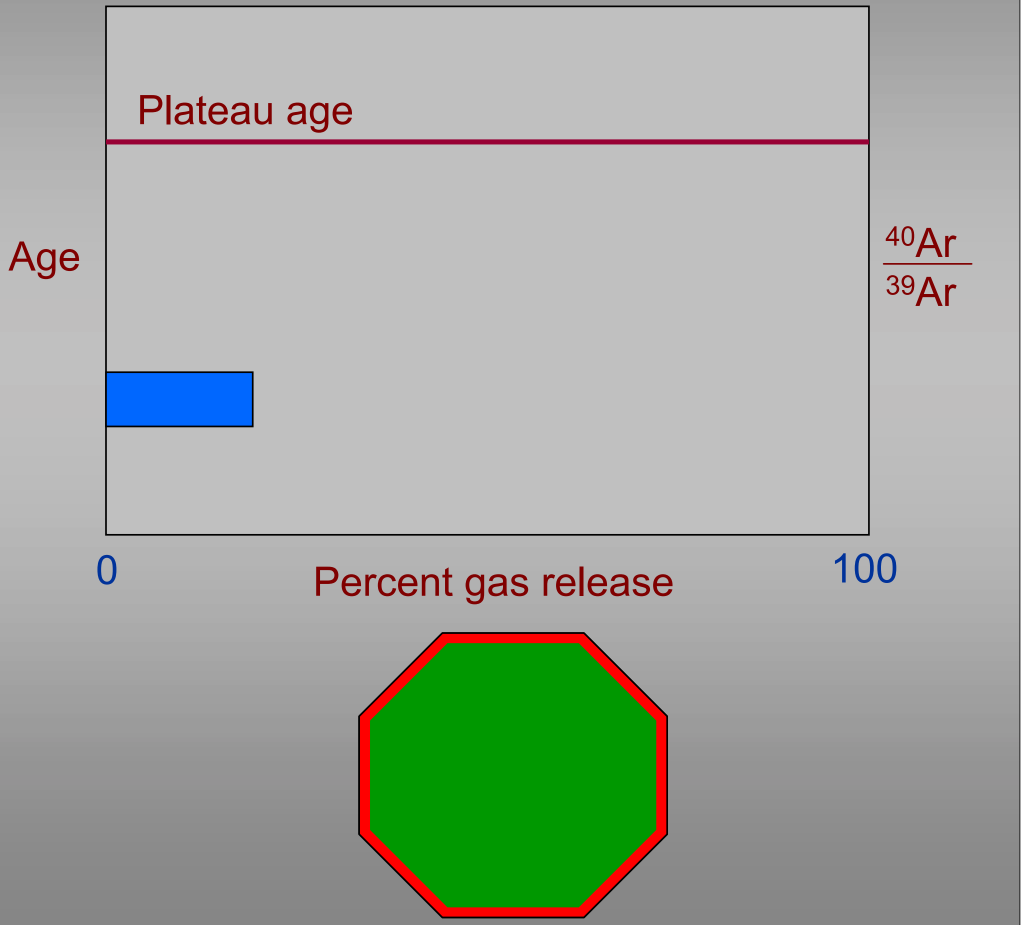
^{39}Ar becomes a proxy for K.



^{40}Ar–^{39}Ar technique

Step heating

Argon is released from progressively more retentive domains



^{40}Ar–^{39}Ar technique

Step heating

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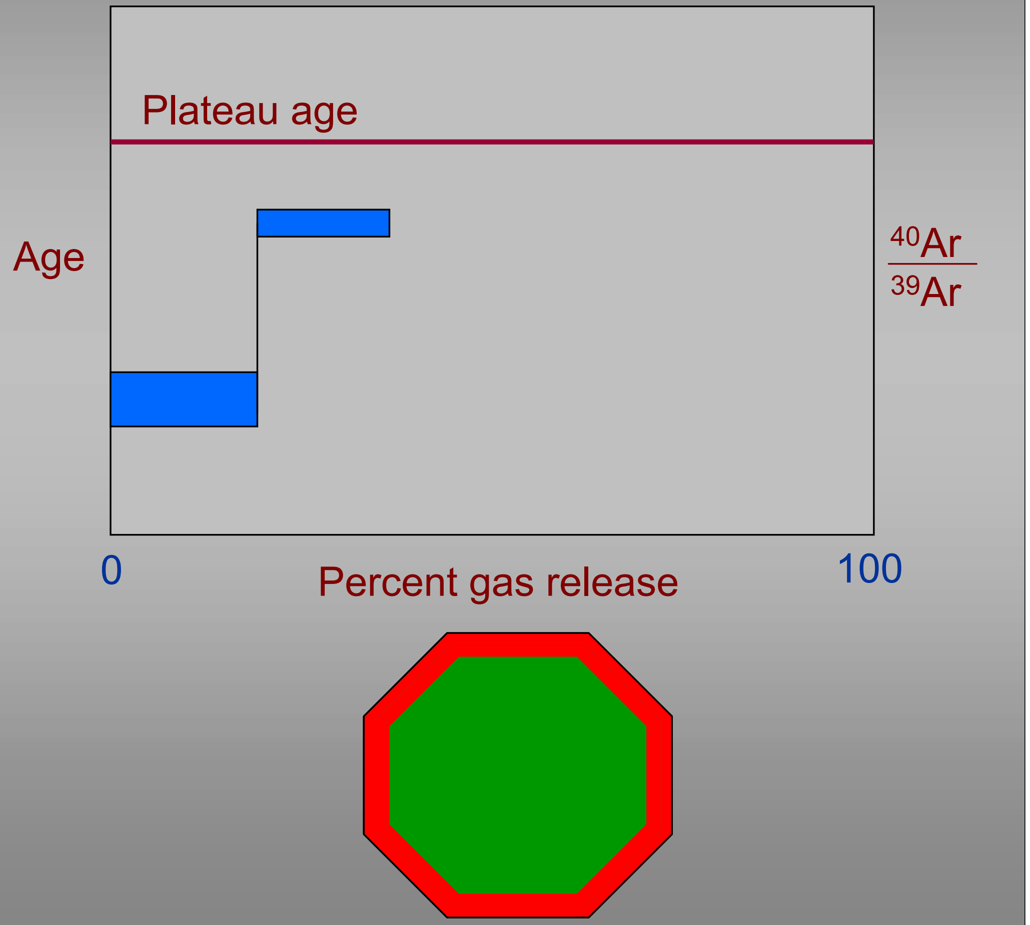
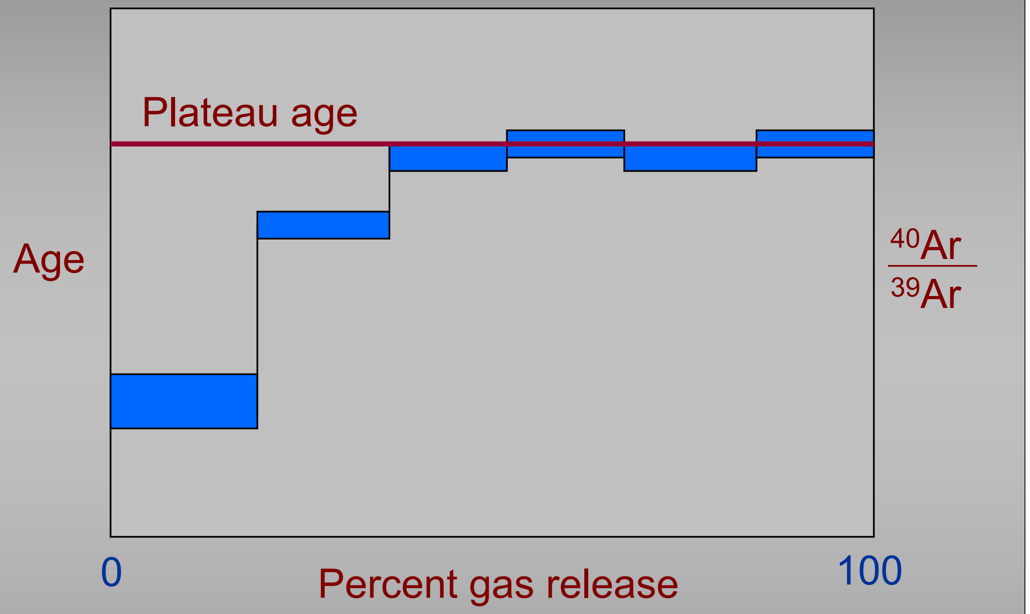


^{40}Ar–^{39}Ar technique

Step heating

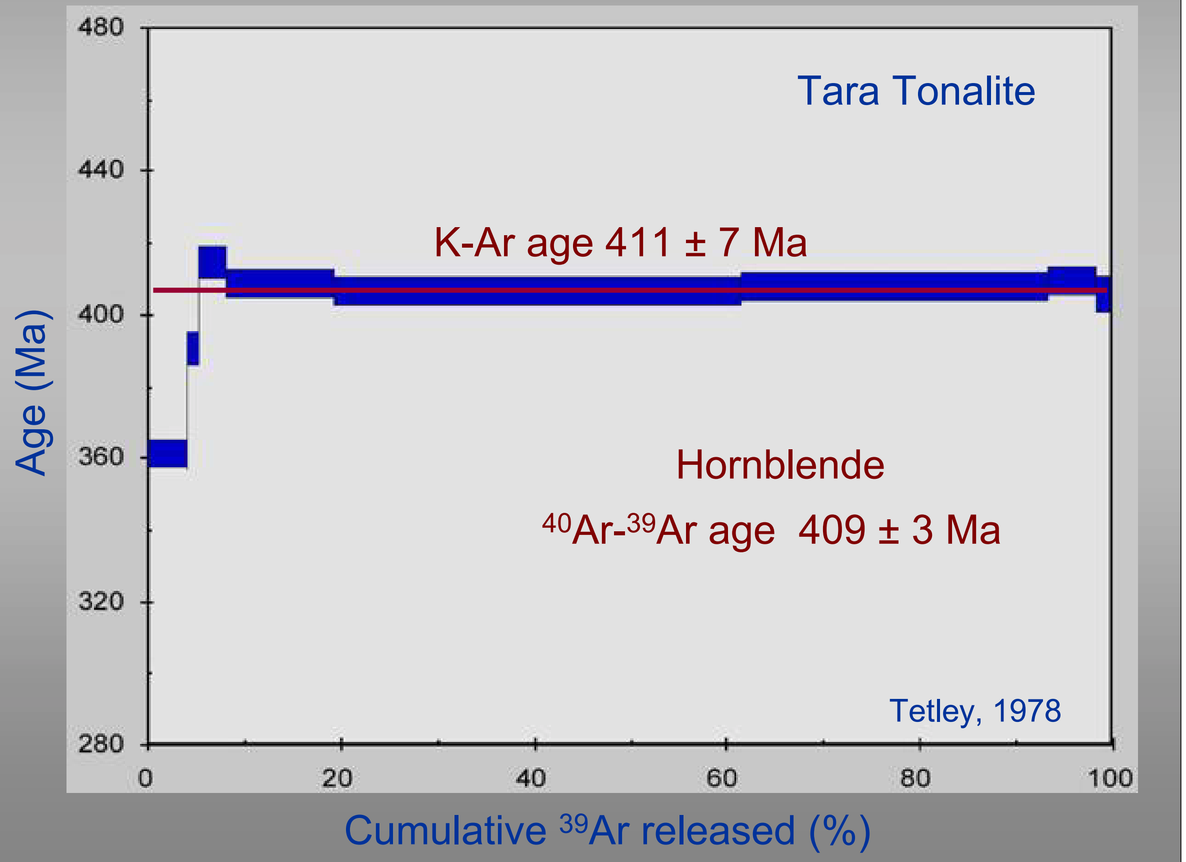
Argon is released from progressively more retentive domains



Eastern Australian granites

^{40}Ar-^{39}Ar

Young I-type Hornblende plateau age agrees well with K-Ar age

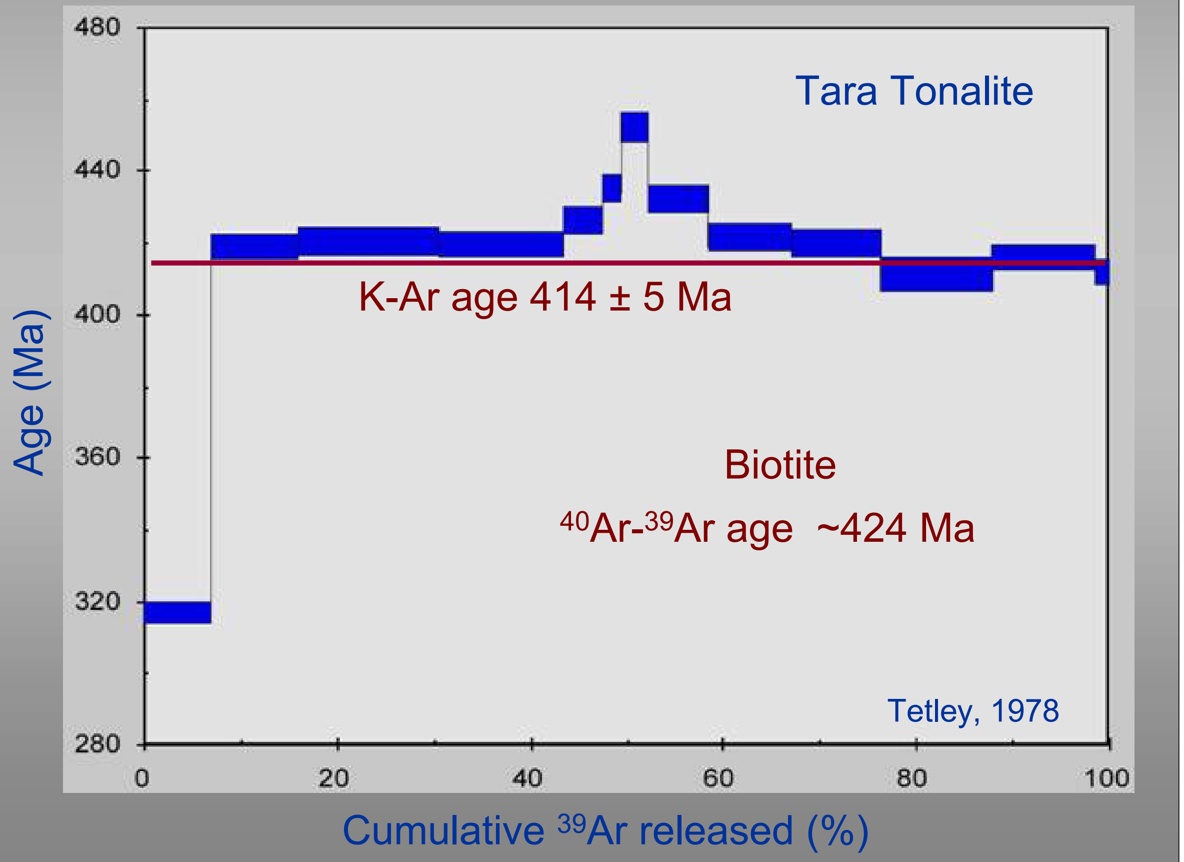


Eastern Australian granites

^{40}Ar-^{39}Ar

Young I-type

Biotite gives an anomalous Ar release pattern

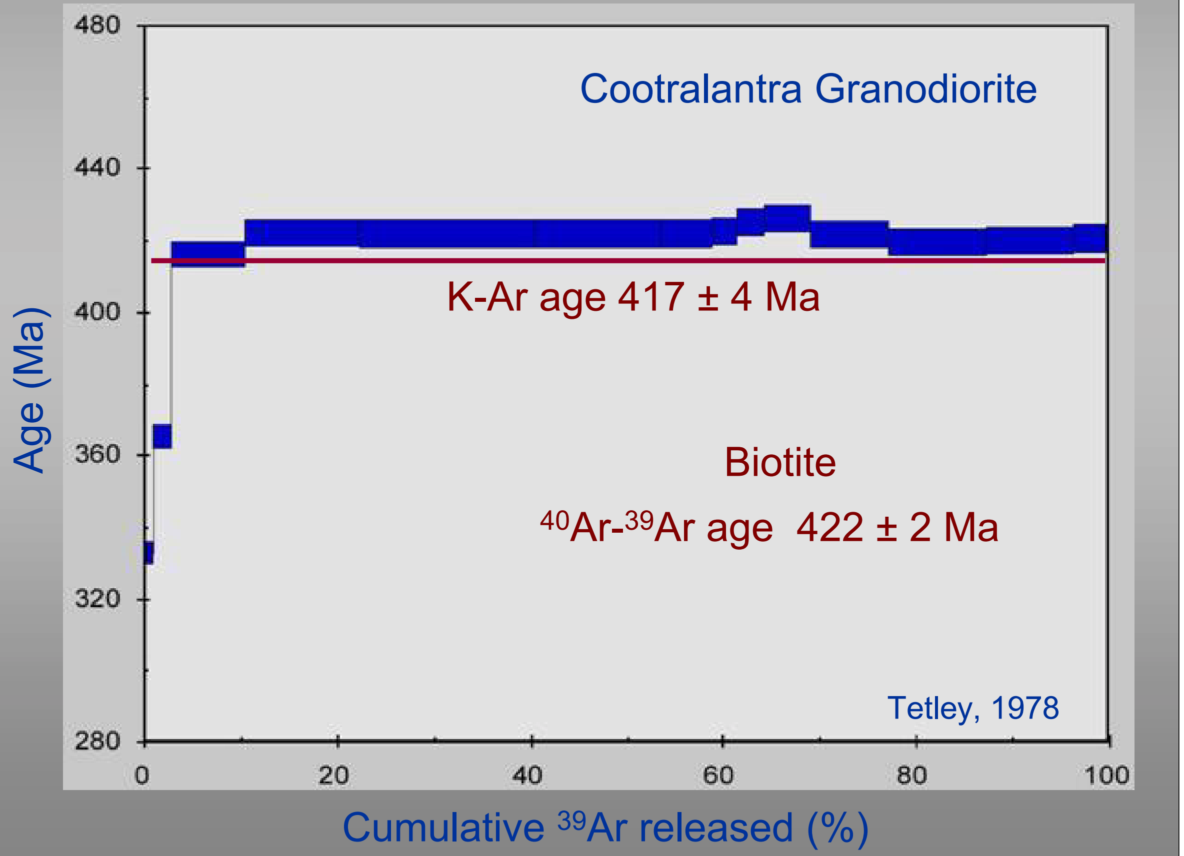


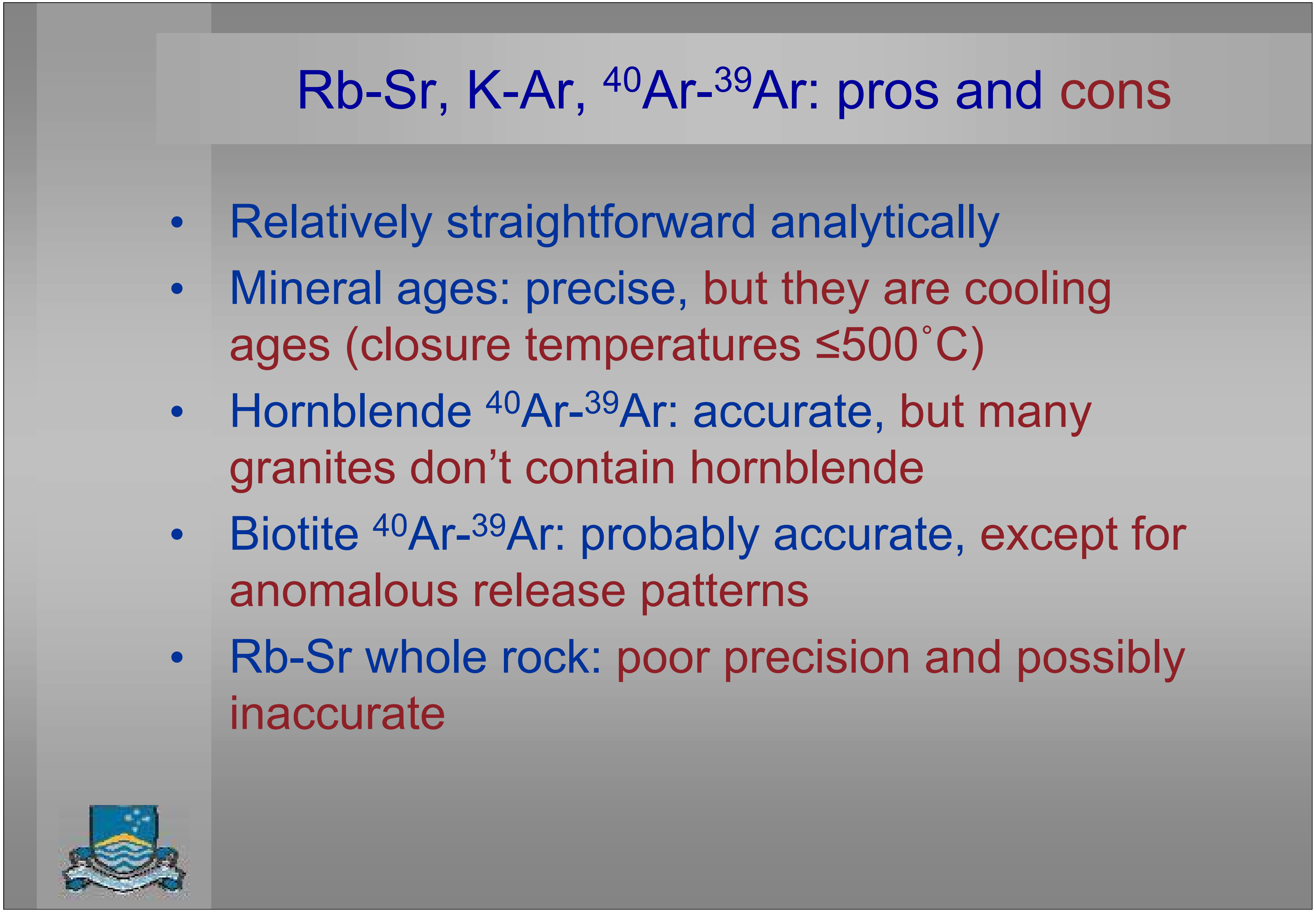
Eastern Australian granites

^{40}Ar-^{39}Ar

Old S-type

Biotite gives a normal Ar release pattern





Rb-Sr, K-Ar, ^{40}Ar-^{39}Ar: pros and cons

- Relatively straightforward analytically
- Mineral ages: precise, but they are cooling ages (closure temperatures ≤500˚C)
- Hornblende ^{40}Ar-^{39}Ar: accurate, but many granites don’t contain hornblende
- Biotite ^{40}Ar-^{39}Ar: probably accurate, except for anomalous release patterns
- Rb-Sr whole rock: poor precision and possibly inaccurate

Mineral U-Pb: pros and cons

- High radioactive parent content
- Low initial daughter content
- High closure temperatures (e.g. >900˚C)
- Isotope Dilution gives exceptional analytical precision (~0.03%)
- Loss of radiogenic daughter is detectable
- Low abundance host minerals (e.g. zircon, monazite)
- Difficult chemistry
- Difficult mass spectrometry

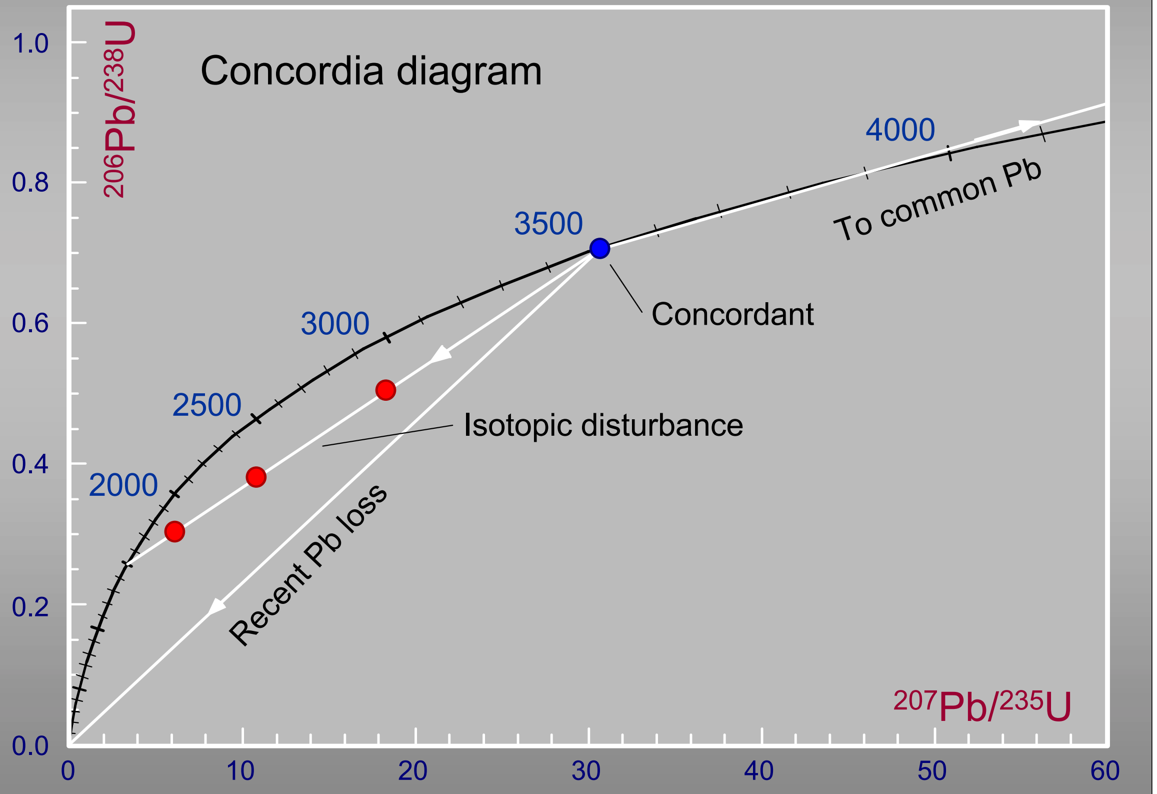
U-Pb

U-Pb is a paired decay scheme

	Half life
$^{238}\mathrm{U} \longrightarrow {}^{206}\mathrm{Pb}$	4.47 Ga
$^{235}\mathrm{U} \longrightarrow {}^{207}\mathrm{Pb}$	704 Ma

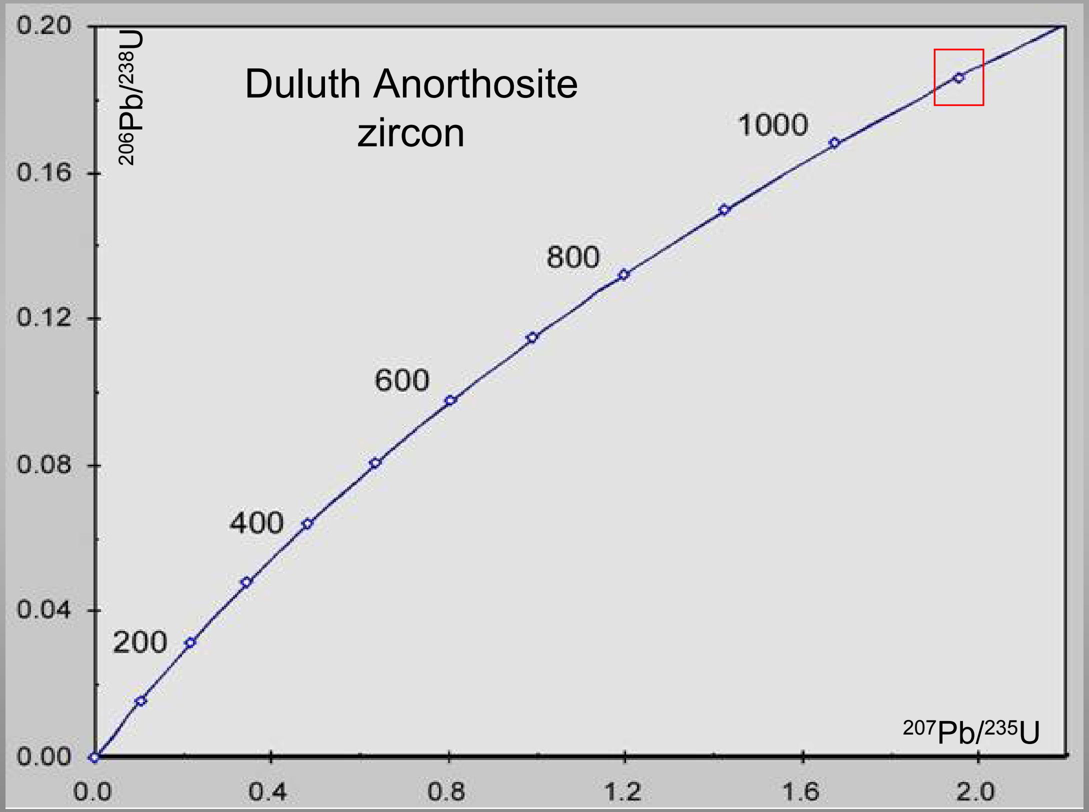
U-Pb

Loss of radiogenic daughter can be detected as discordance



U-Pb

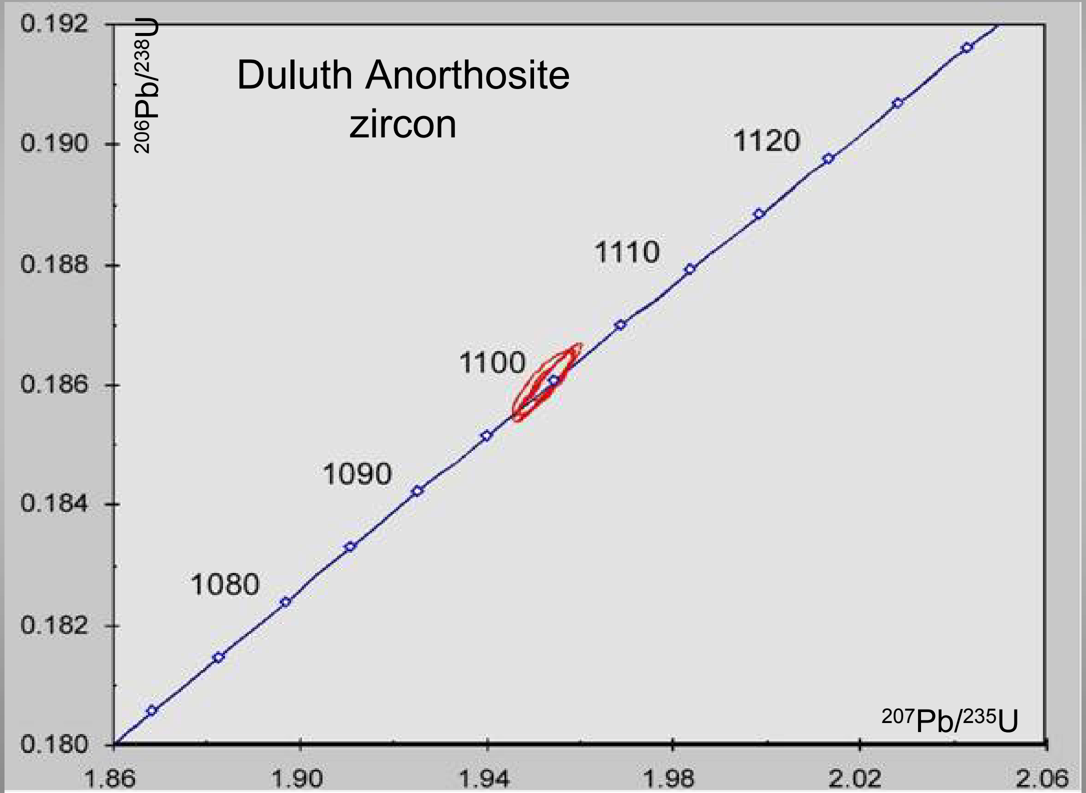
Isotope Dilution U-Pb age measurements can be very precise



Paces & Miller, 1993

U-Pb

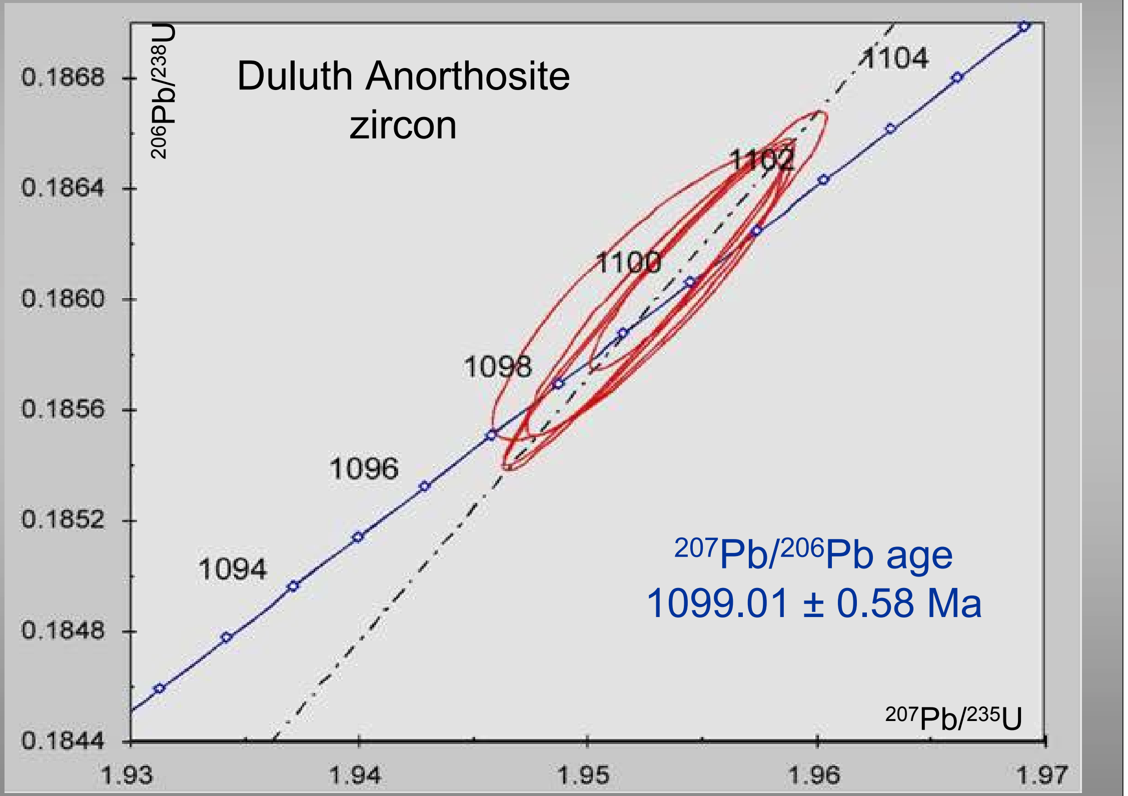
Isotope Dilution U-Pb age measurements can be very precise



Paces & Miller, 1993

U-Pb

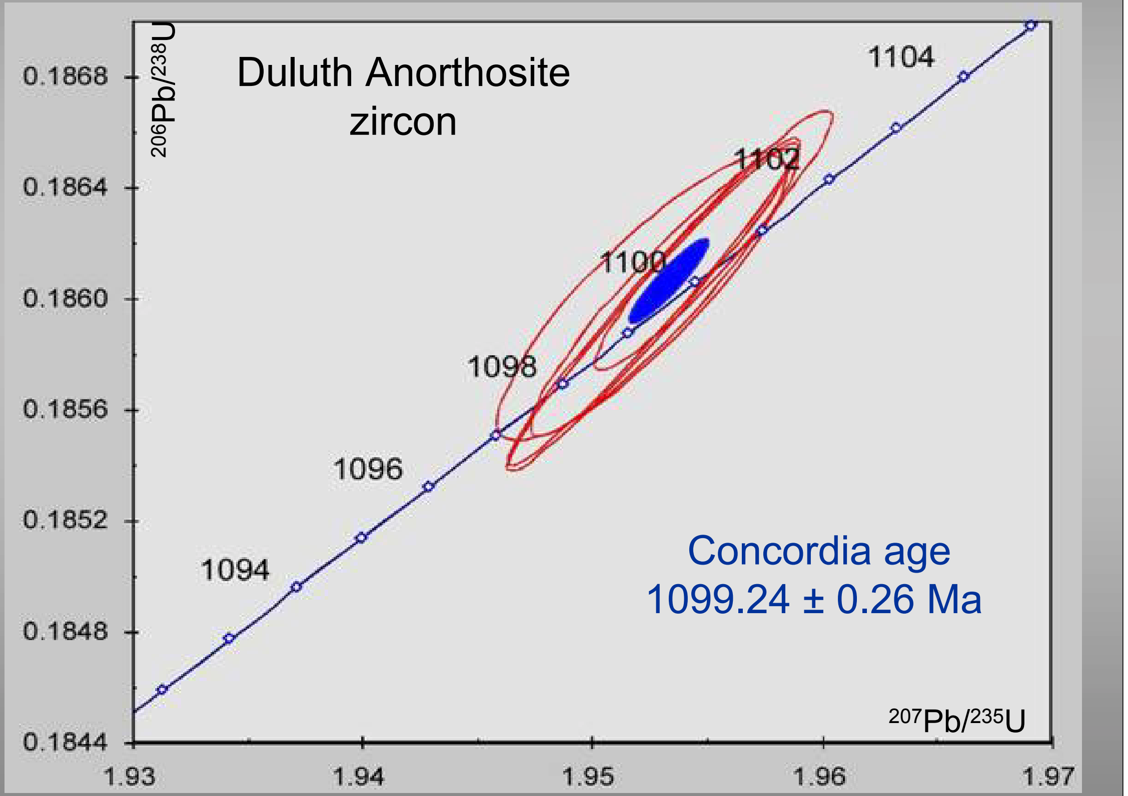
Isotope Dilution U-Pb age measurements can be very precise



Paces & Miller, 1993

U-Pb

Isotope Dilution U-Pb age measurements can be very precise

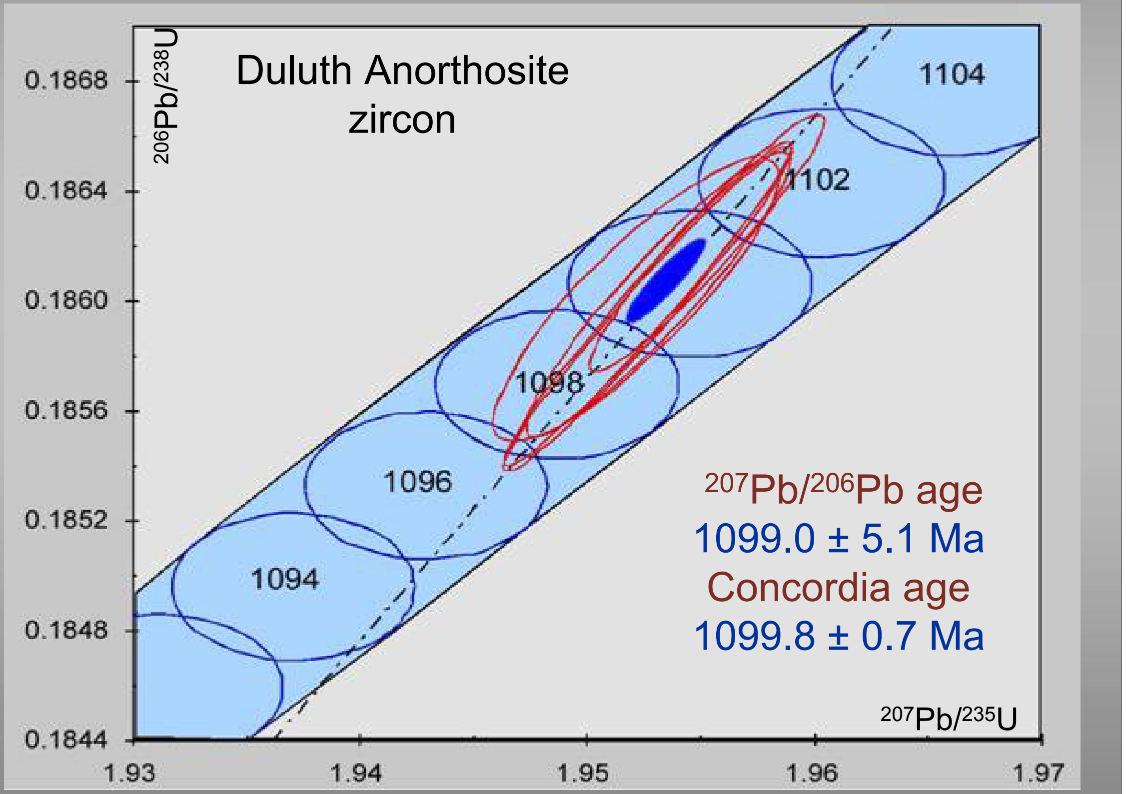


Paces & Miller, 1993

U-Pb

Isotope Dilution

Accuracy now limited by uncertainty in the decay constants



$^{207}Pb/^{206}Pb$ age 1099.0 ± 5.1 Ma

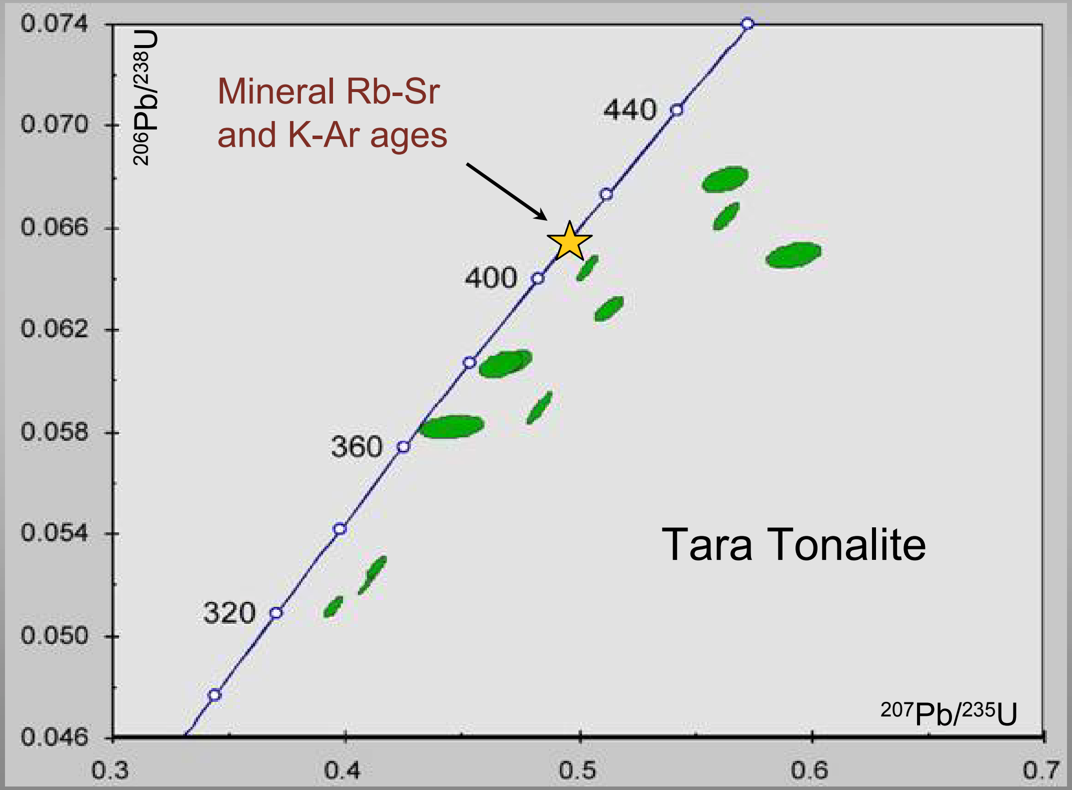
Concordia age 1099.8 ± 0.7 Ma

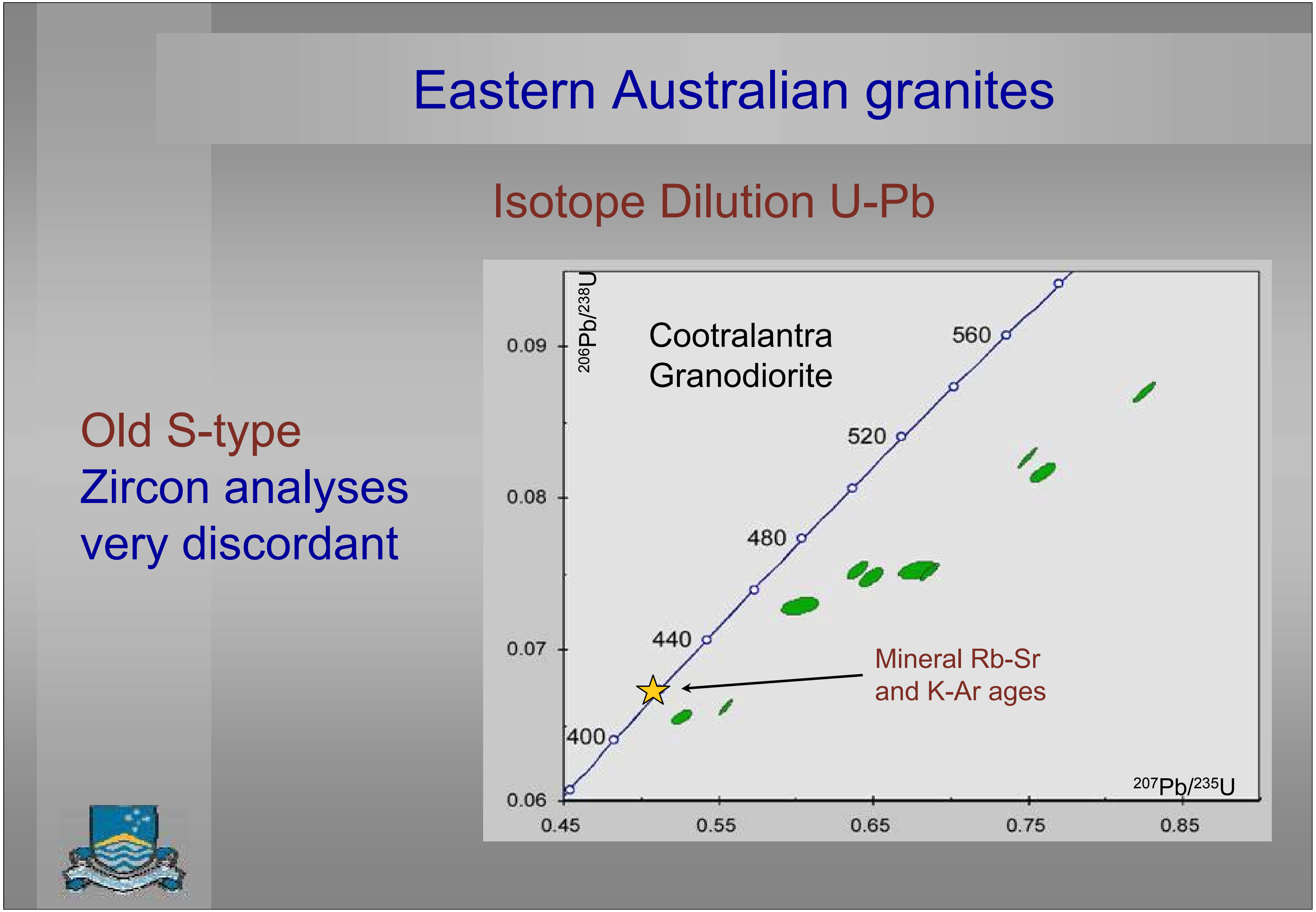
Paces & Miller, 1993

Eastern Australian granites

Isotope Dilution U-Pb

Young I-type
All zircon analyses are discordant





Eastern Australian granites

Isotope Dilution U-Pb

Old S-type
Zircon analyses
very discordant

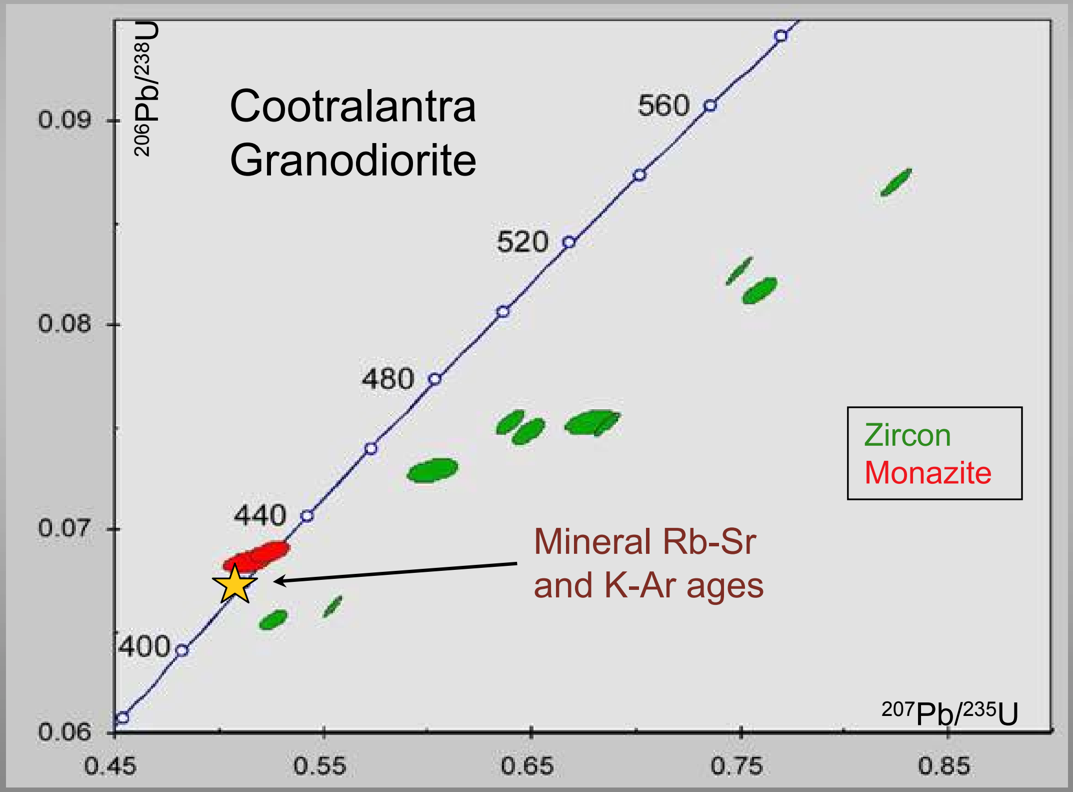
Mineral Rb-Sr
and K-Ar ages

Eastern Australian granites

Isotope Dilution U-Pb

Old S-type

Zircon analyses very discordant, but monazite analyses are not

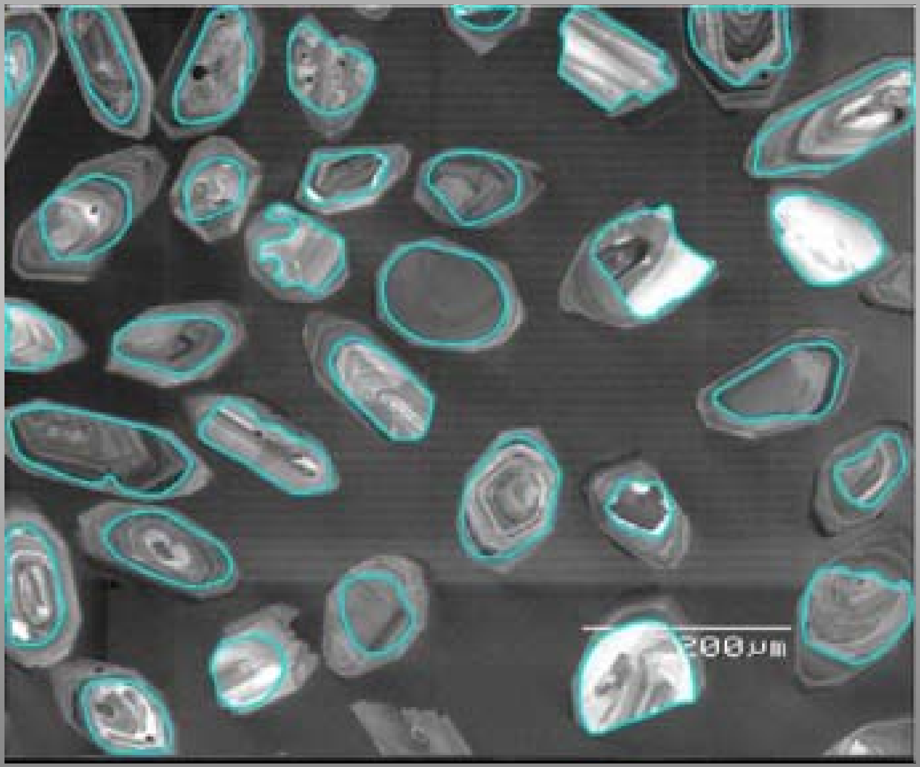


Cootralantra Granodiorite

Mineral Rb-Sr and K-Ar ages

Eastern Australian granites

U-Pb



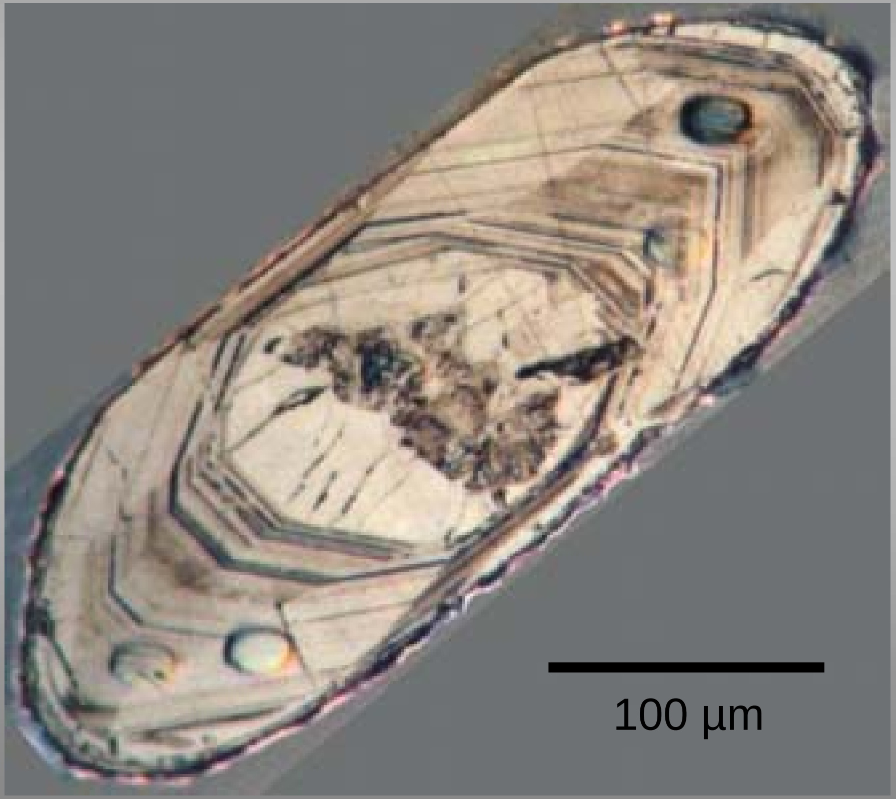
Old S-type

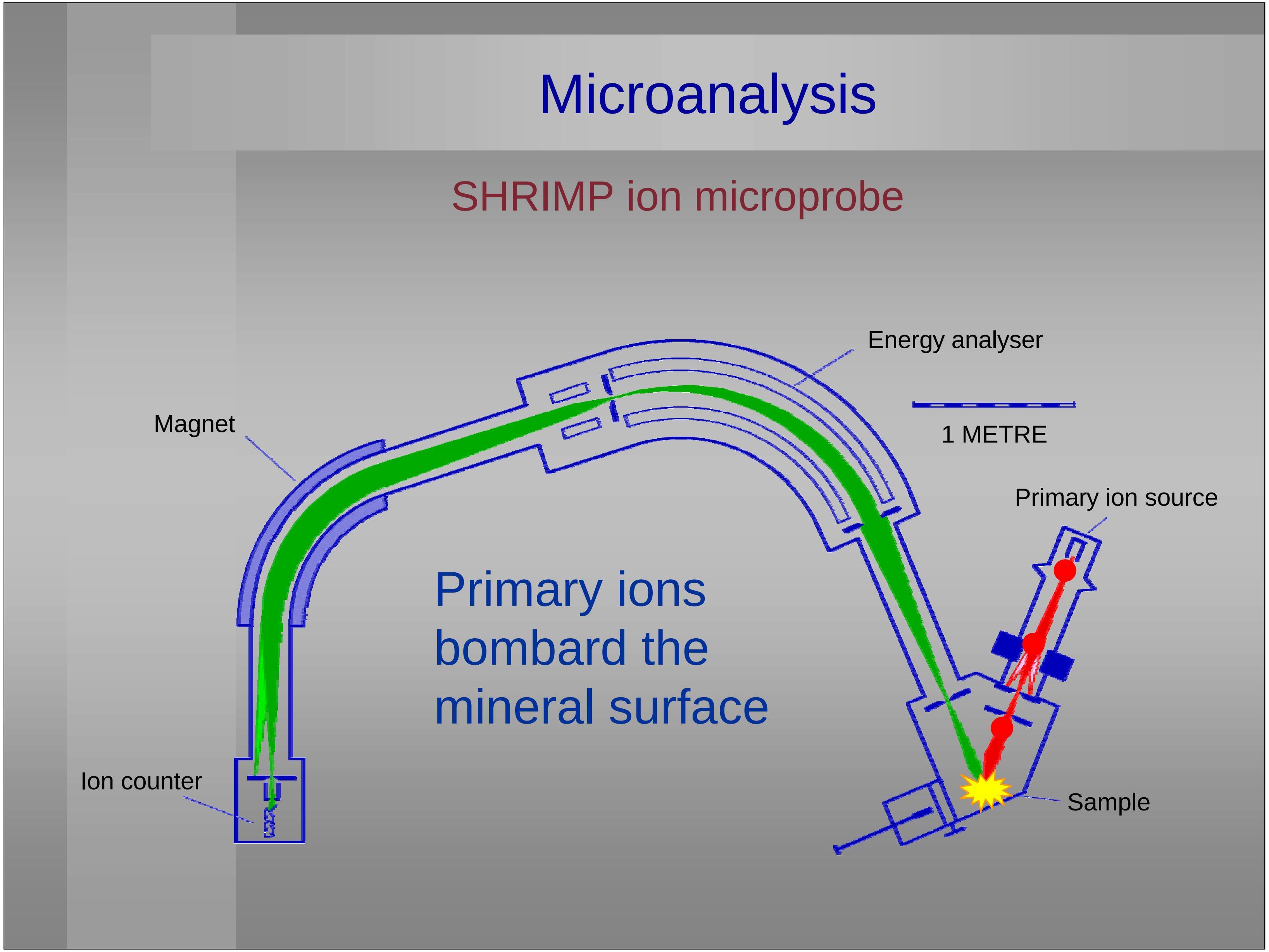
Virtually every zircon grain contains an inherited core

Microanalysis

Ion Microprobe

Single generations of mineral growth can be dated





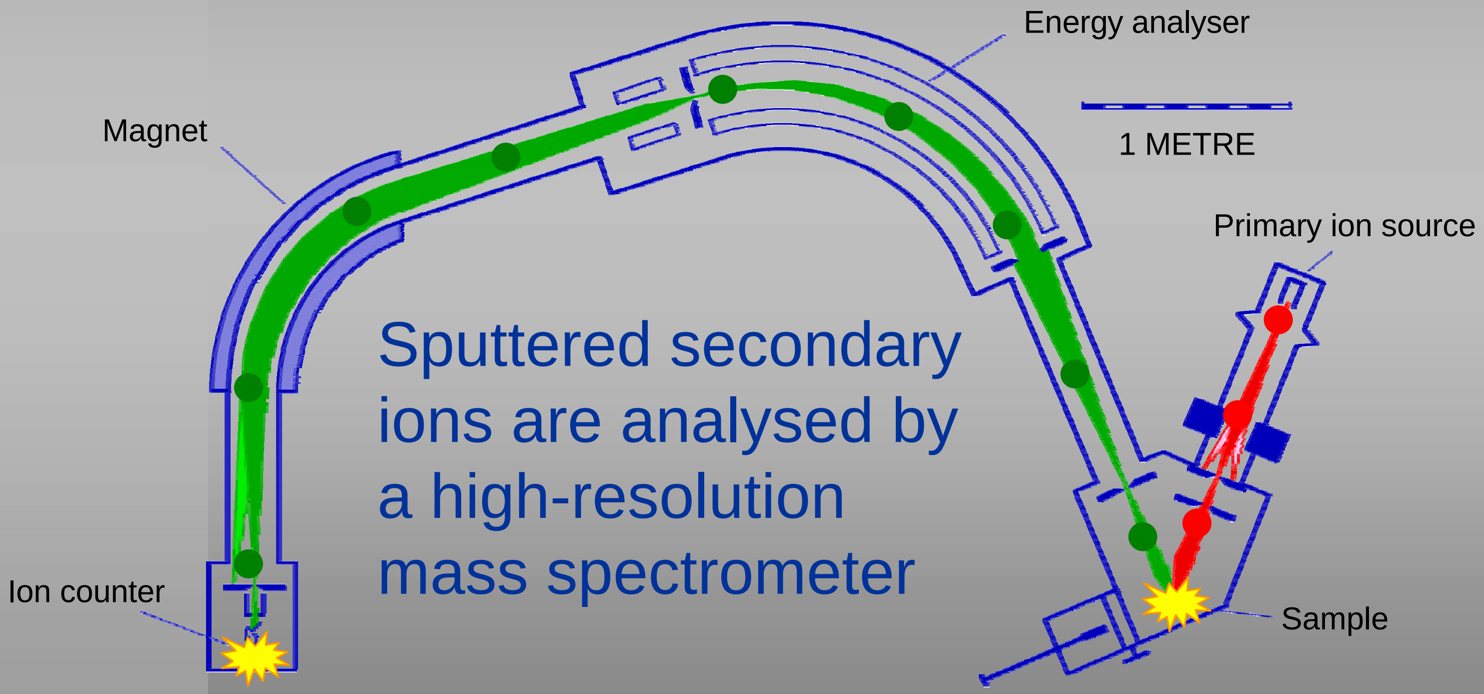
Microanalysis

SHRIMP ion microprobe

Primary ions bombard the mineral surface

Microanalysis

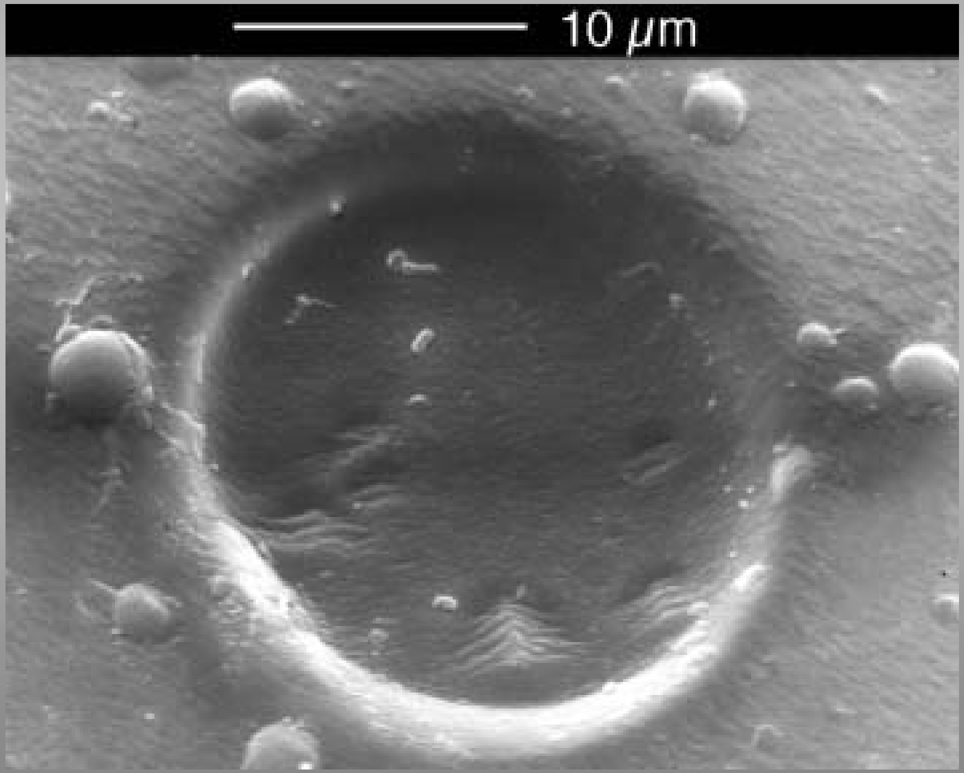
SHRIMP ion microprobe



Sputtered secondary ions are analysed by a high-resolution mass spectrometer

Microanalysis

SHRIMP ion microprobe

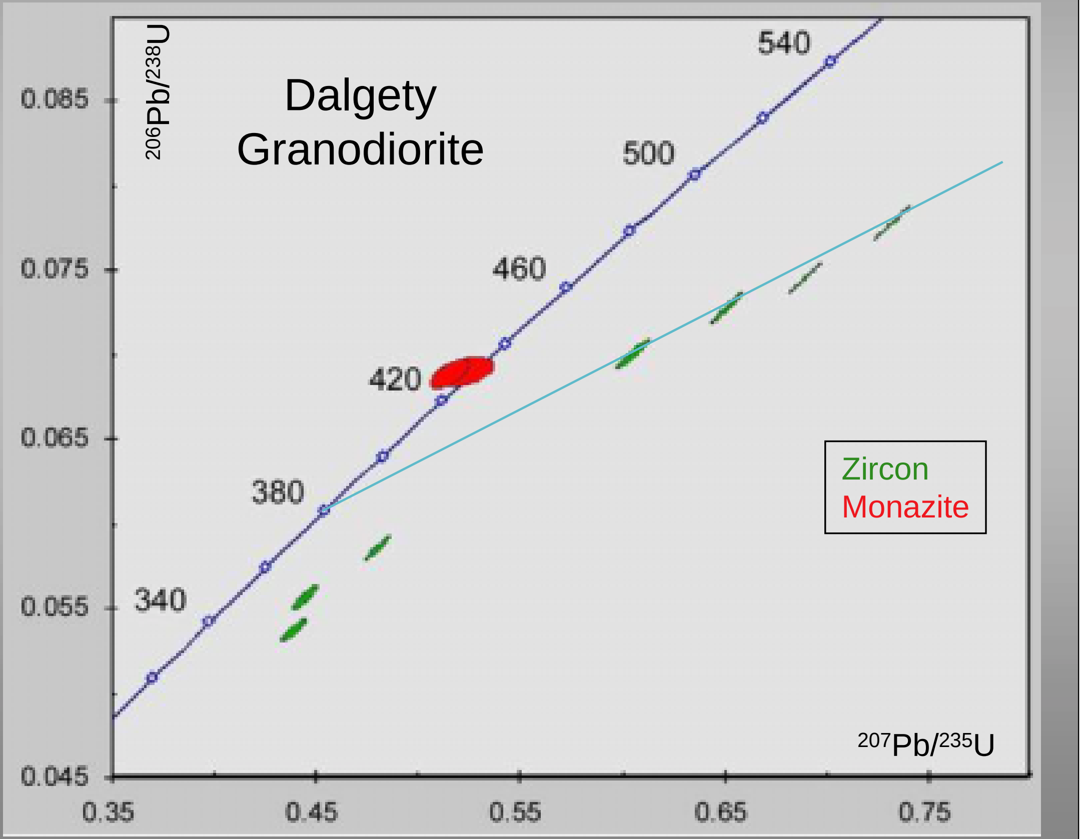


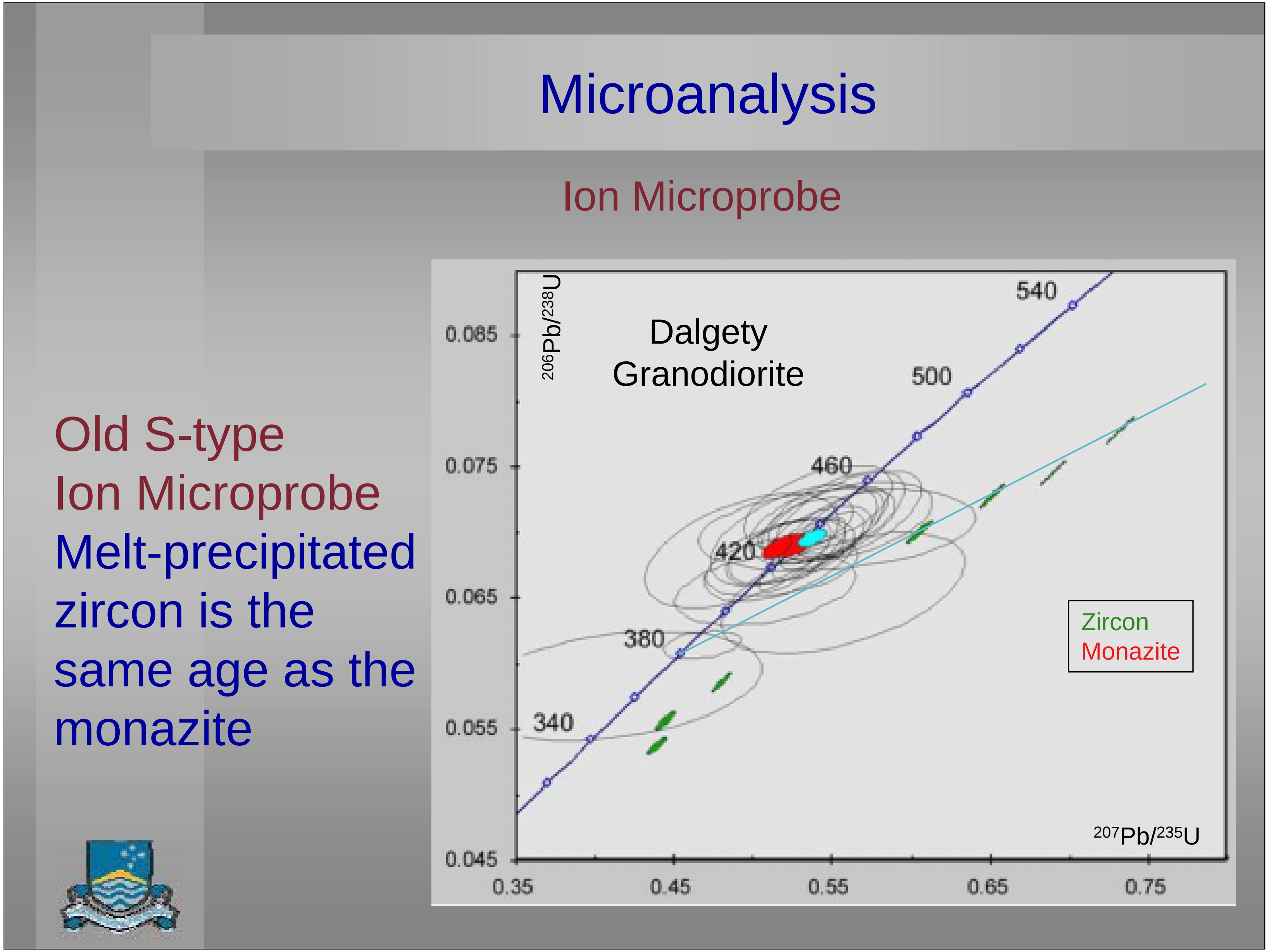
After the analysis the pit is about 2 μm deep

Microanalysis

Ion Microprobe

Old S-type
Isotope Dilution
Monazite older
than inferred
zircon age





Microanalysis

Ion Microprobe

Old S-type
Ion Microprobe
Melt-precipitated zircon is the same age as the monazite

Microanalysis

Laser Ablation ICP-MS

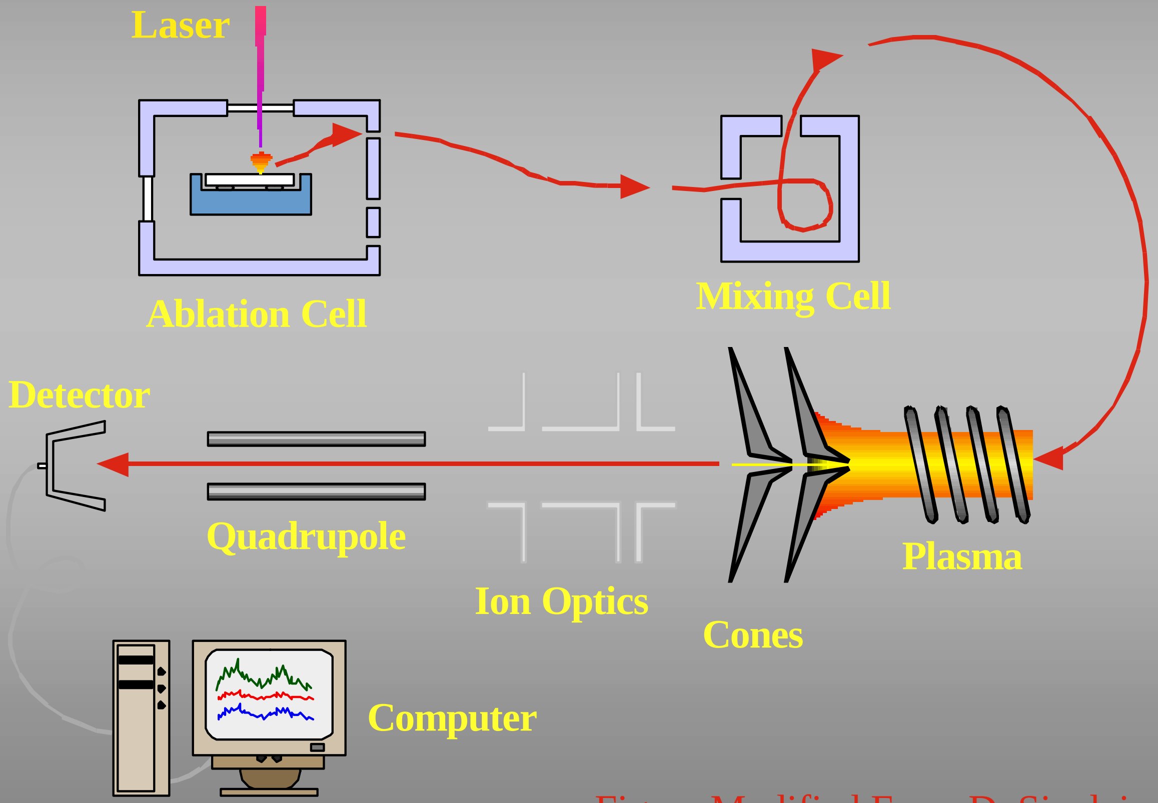
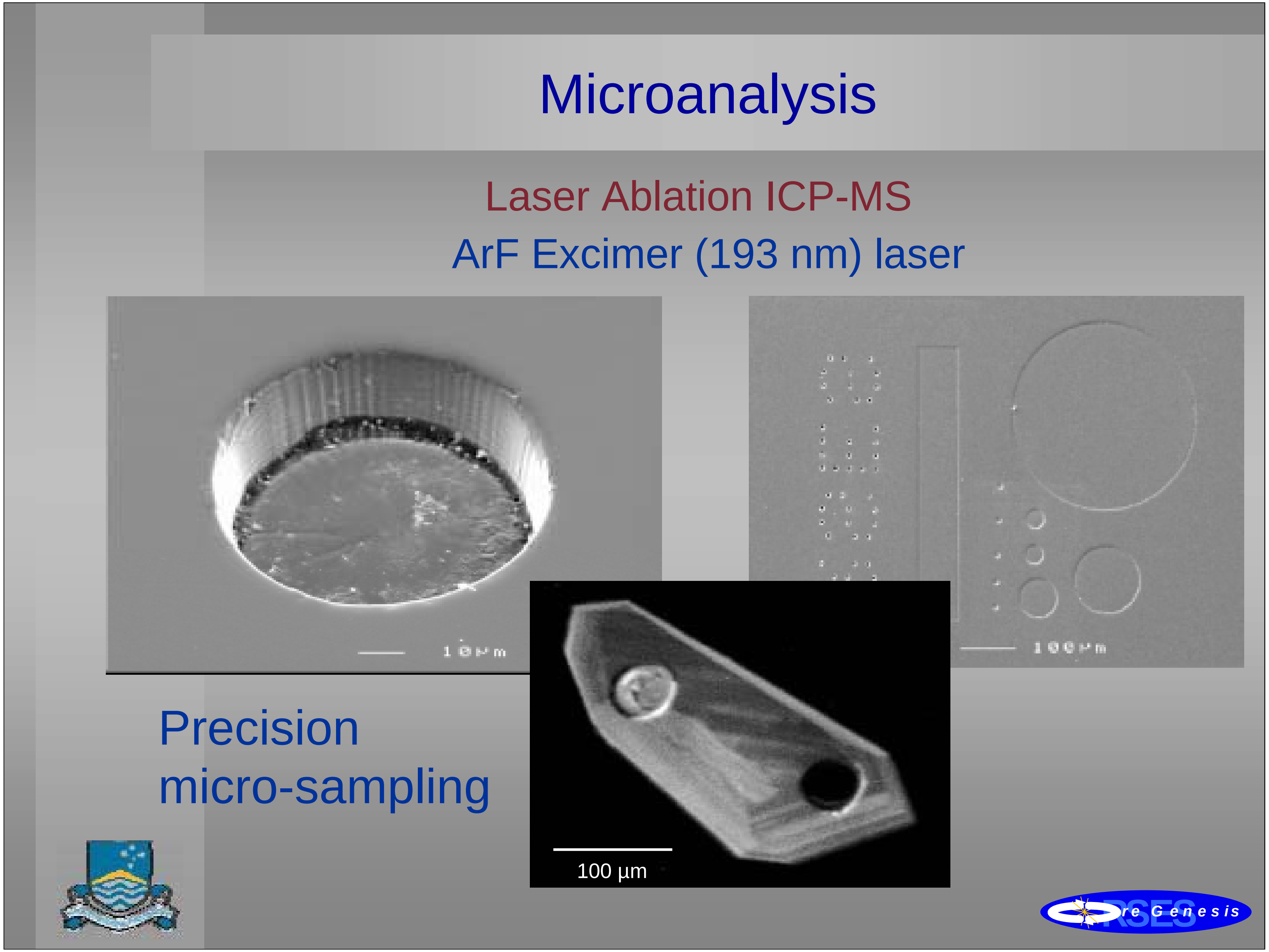


Figure Modified From D. Sinclair, 199



Microanalysis

Laser Ablation ICP-MS

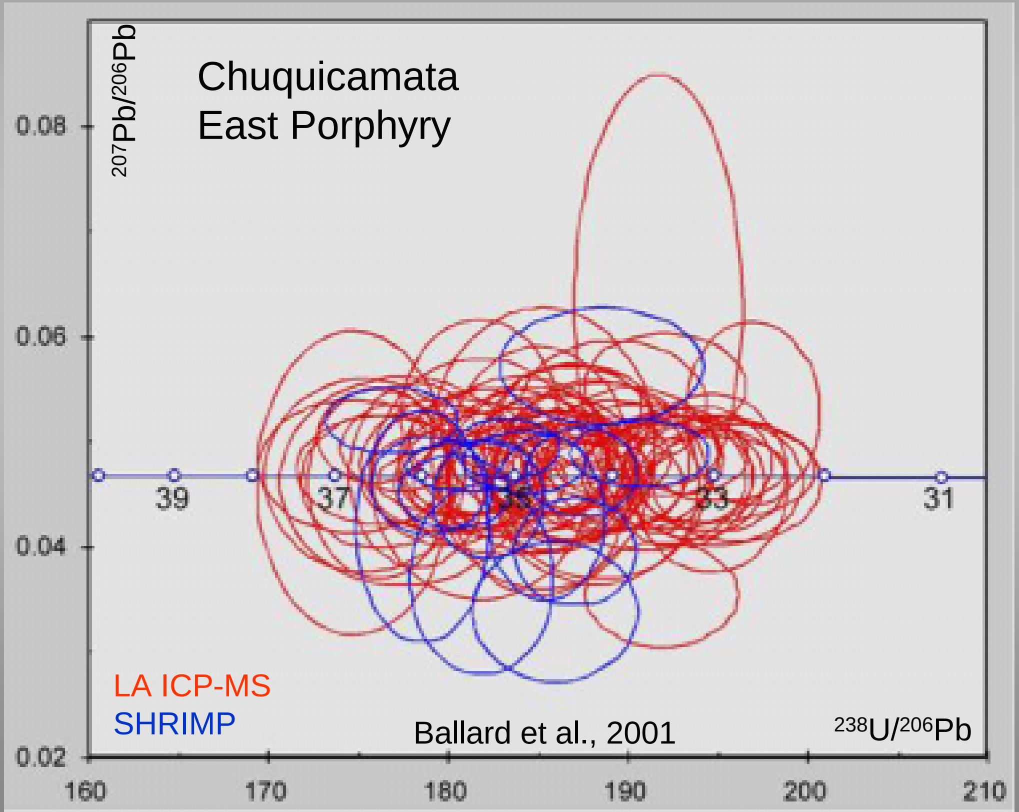
ArF Excimer (193 nm) laser

Precision micro-sampling

Microanalysis

Laser Ablation ICP-MS

Analyses comparable precision to Ion Microprobe



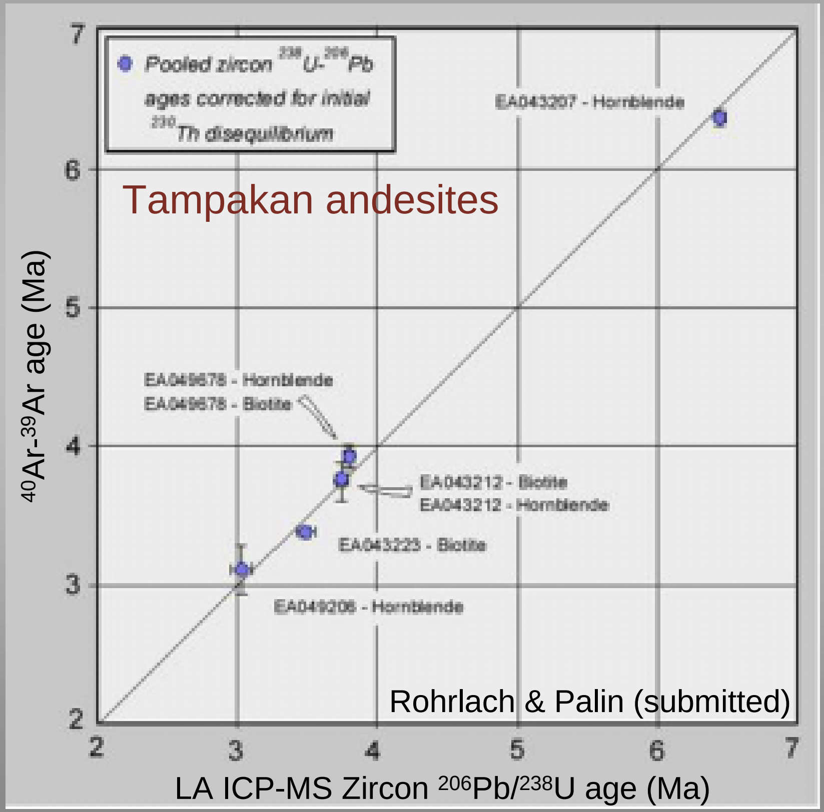
Ballard et al., 2001

Microanalysis

The question of accuracy

Laser Ablation ICP-MS

Accuracy comparable to ^{40}Ar-^{39}Ar



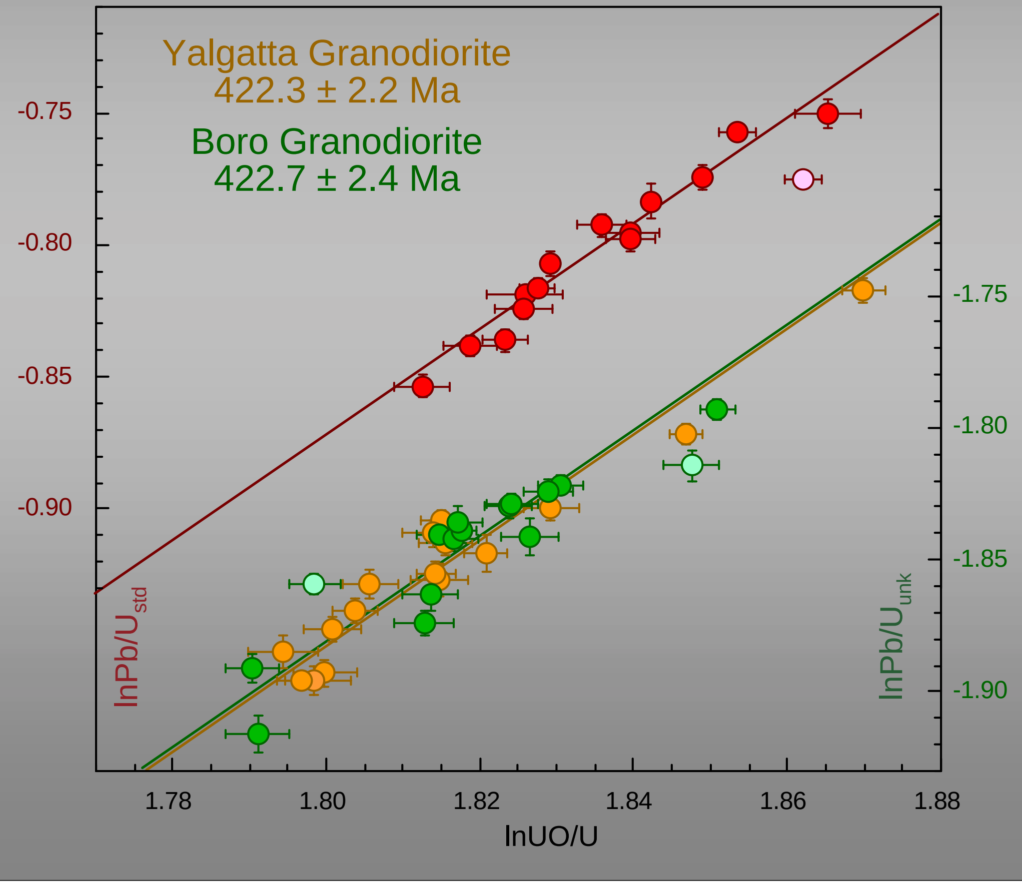
Tampakan andesites

Rohrlach & Palin (submitted)

Microanalysis

The question of accuracy

Ion Microprobe
Pb/U calibration
against
a standard

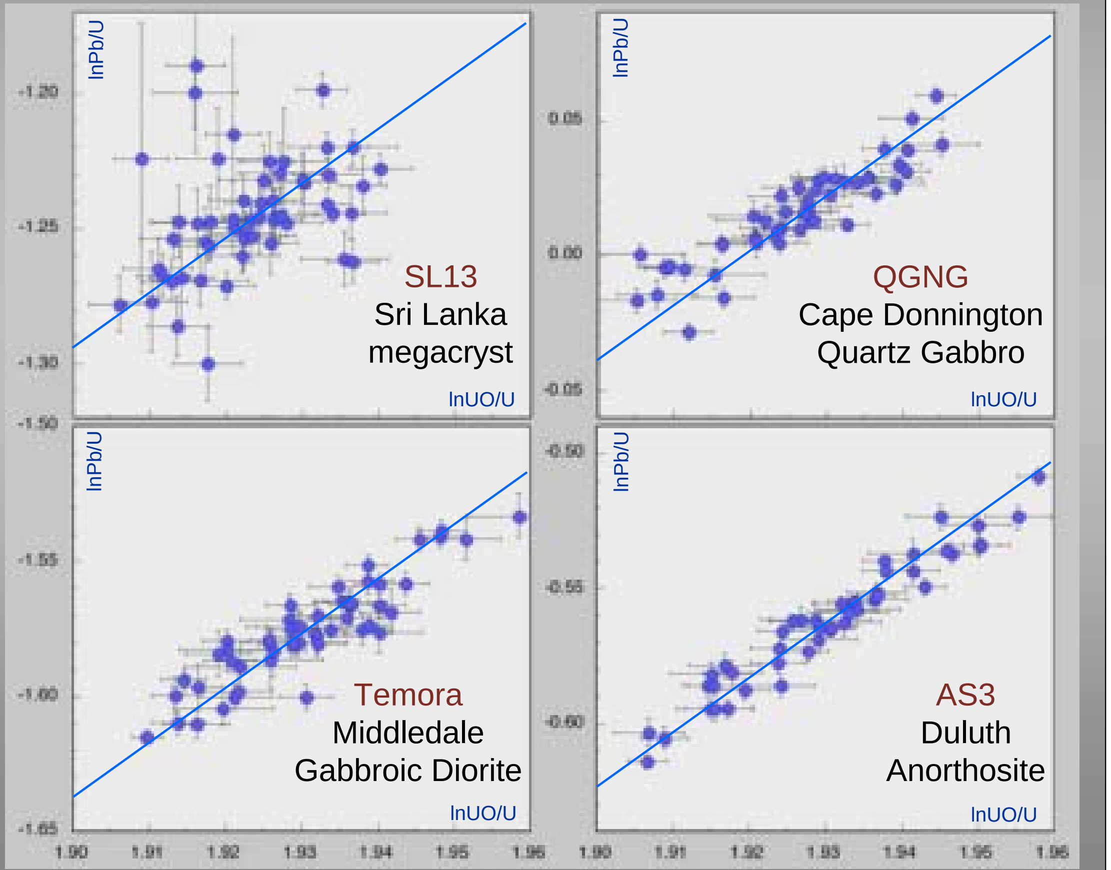


Microanalysis

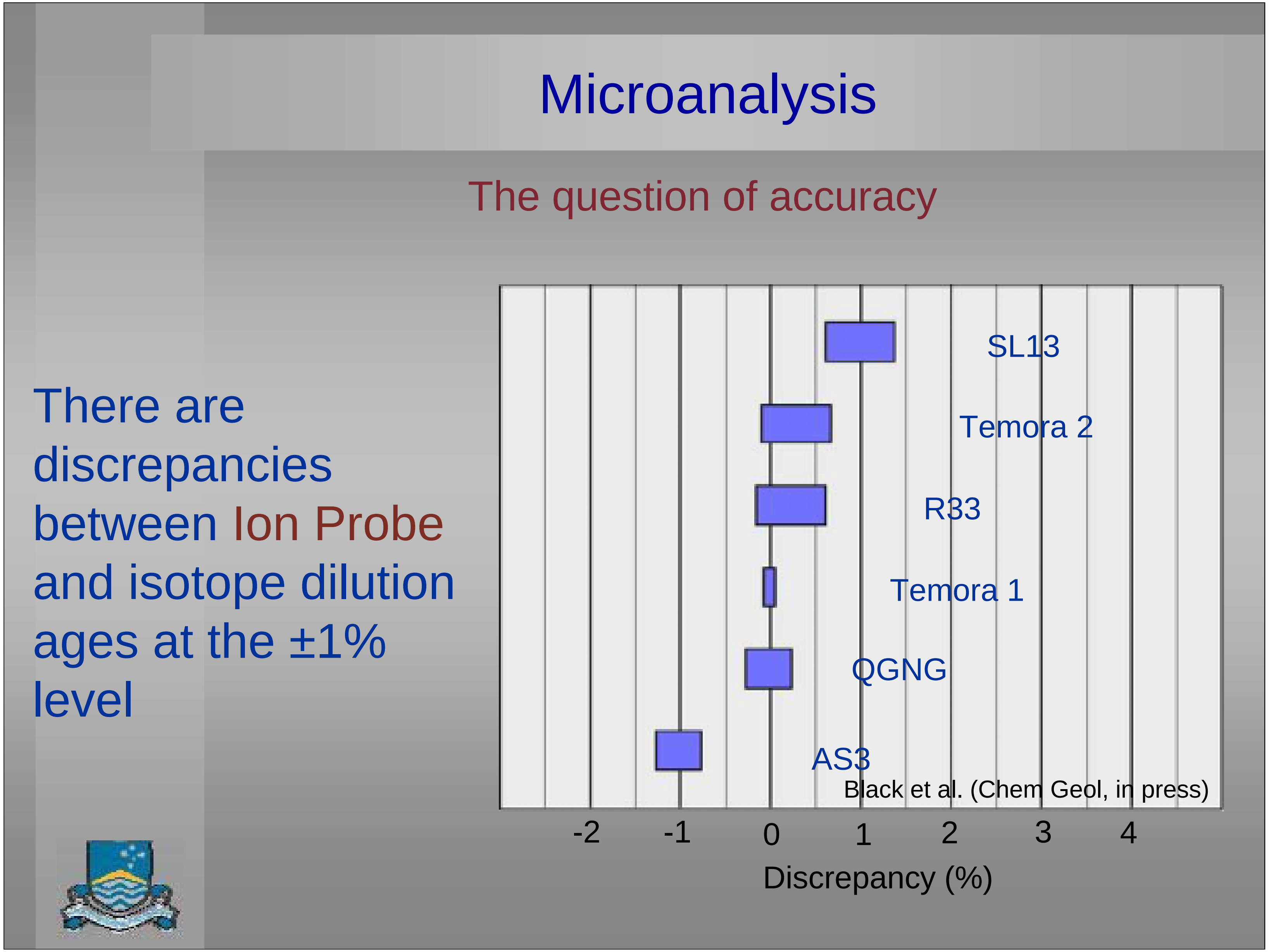
The question of accuracy

Ion Microprobe

Finding homogeneous standards is not easy



Black et al. (Chem Geol, in press)

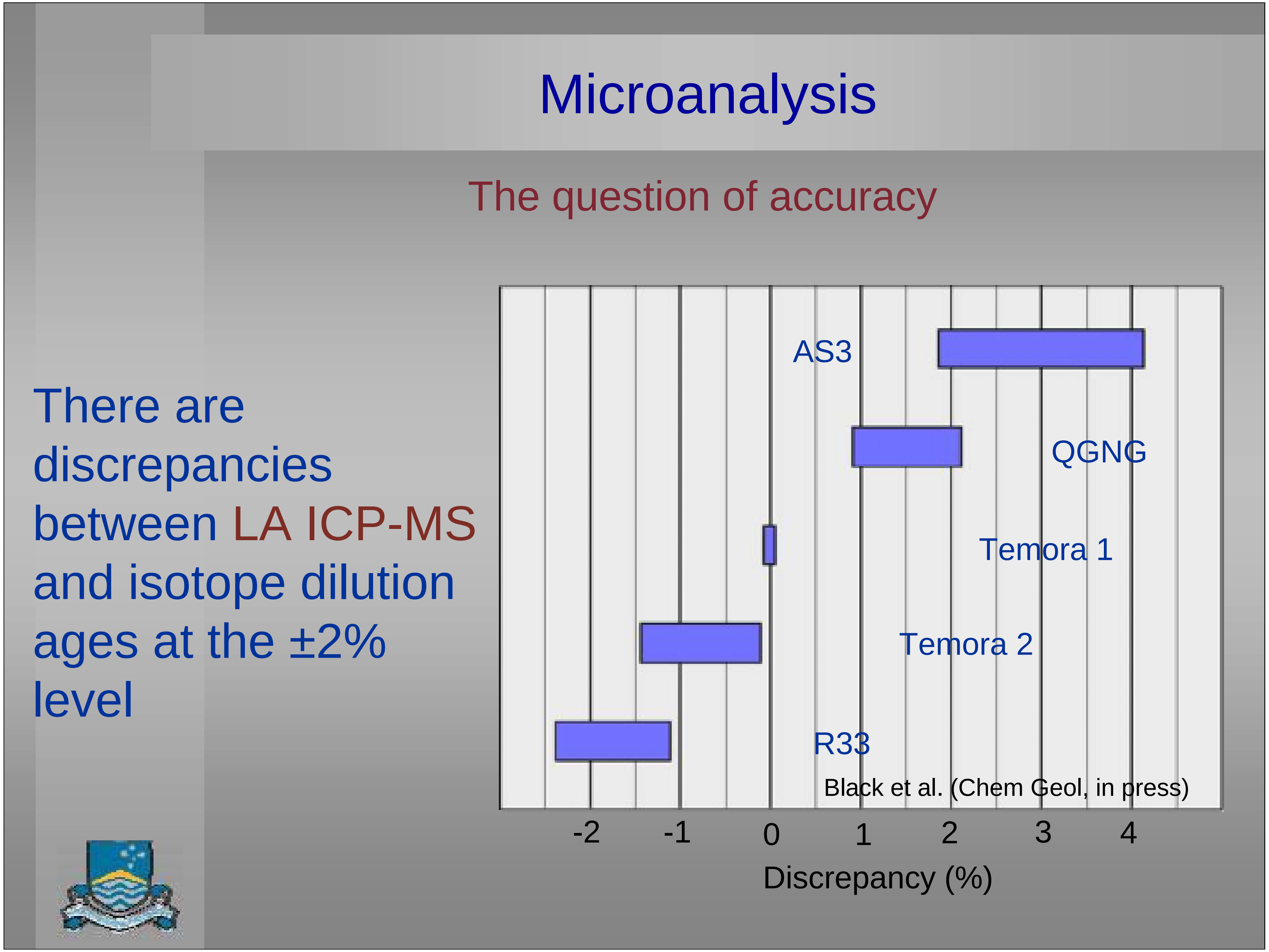


Microanalysis

The question of accuracy

There are discrepancies between Ion Probe and isotope dilution ages at the ±1% level

Black et al. (Chem Geol, in press)



Microanalysis

The question of accuracy

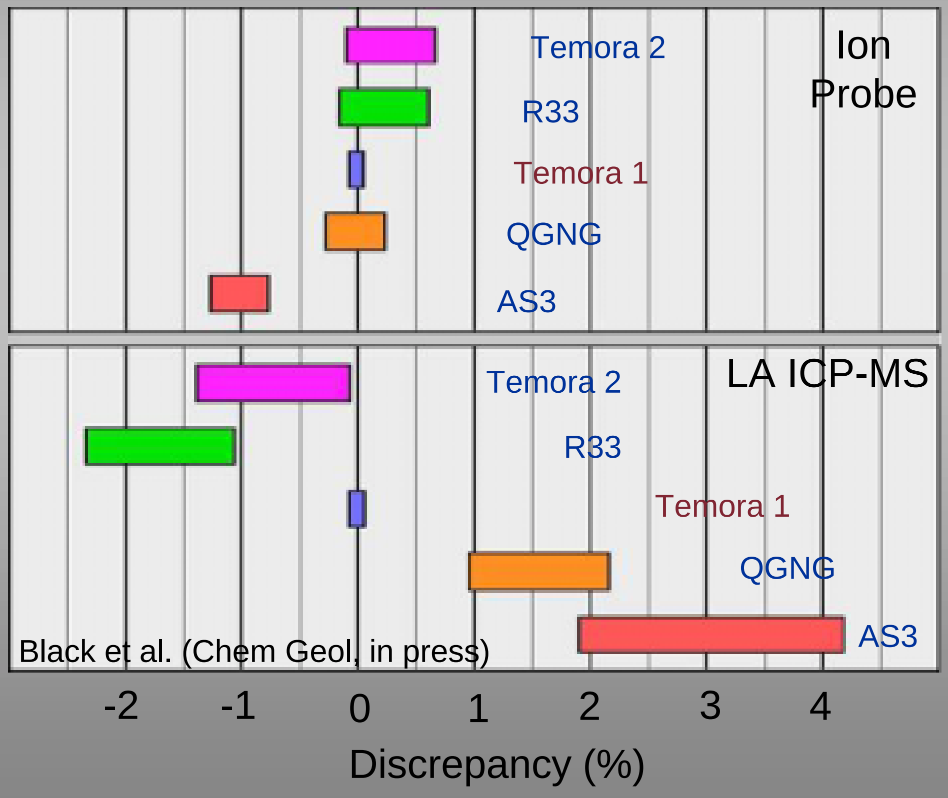
There are discrepancies between LA ICP-MS and isotope dilution ages at the ±2% level

Black et al. (Chem Geol, in press)

Microanalysis

The question of accuracy

The discrepancies for Ion Probe and LA ICP-MS are not in the same direction



Black et al. (Chem Geol, in press)

Meeting the challenge to get the ages right

1. Rb-Sr, K-Ar and Ar-Ar mineral ages record cooling below 500–350˚C.
2. In large batholiths, cooling below 350˚C can occur long after granite emplacement.
3. Whole rock Rb-Sr ages are imprecise, and can be inaccurate if the initial Sr isotopic composition of a magma is not uniform.
4. U-Pb Isotope Dilution analyses are extremely precise, but zircon and monazite U-Pb ages record granite emplacement only in the absence of inheritance.
5. U-Pb microanalyses are relatively imprecise, but melt-precipitated zircon and monazite can be dated free from the effects of inheritance.
6. When no inheritance is present, the uncertainty in Isotope Dilution U-Pb ages is determined mainly by uncertainty in the U decay constants.
7. The accuracy of Pb/U ages measured by microanalysis is presently limited by calibration factors to 1-3%.