Operating variables impacting U-Pb reproducibility

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Content

Operating variables impacting U-Pb reproducibility – *how do issues such as pulse energy, focus, water vapour in the cell and resin mount degassing impact U-Pb data?*

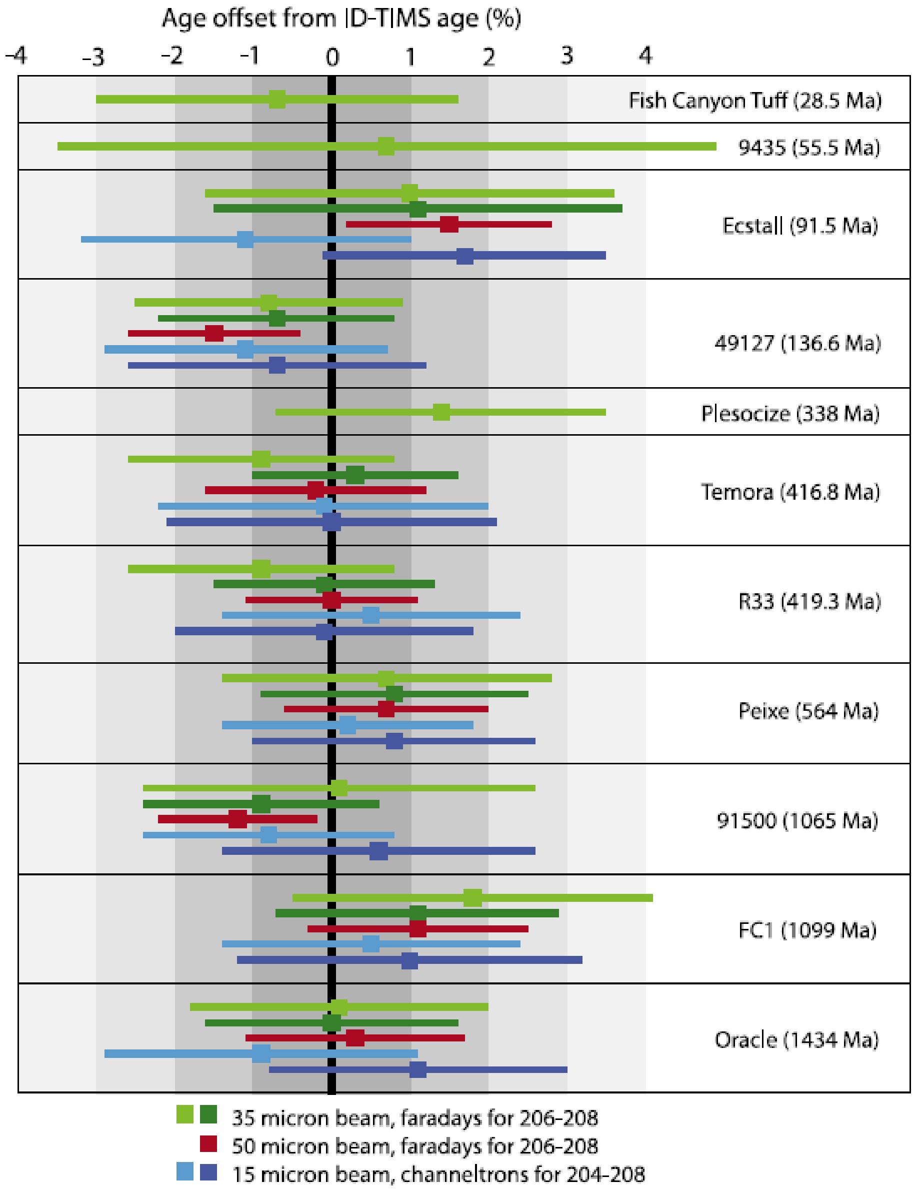
1. Operating parameters
    1. Laser energy (fluence)
    2. Spot size
    3. Laser focus (10 and 16x demagnification)
2. Sample and cell degassing/desorption
    1. Moisture desorption in large-format sample cells
    2. Sample degassing (Jay Thompson)

LA-ICP-MS U-Pb zircon dating limitations

Matrix-related Pb/U fractionation:

"……it would seem that any LA-ICP-MS zircon U-Pb and $^{207}Pb/^{206}Pb$ age determination cannot be meaningfully interpreted at below a ca. 3% to 4% (2 RSD) confidence level."

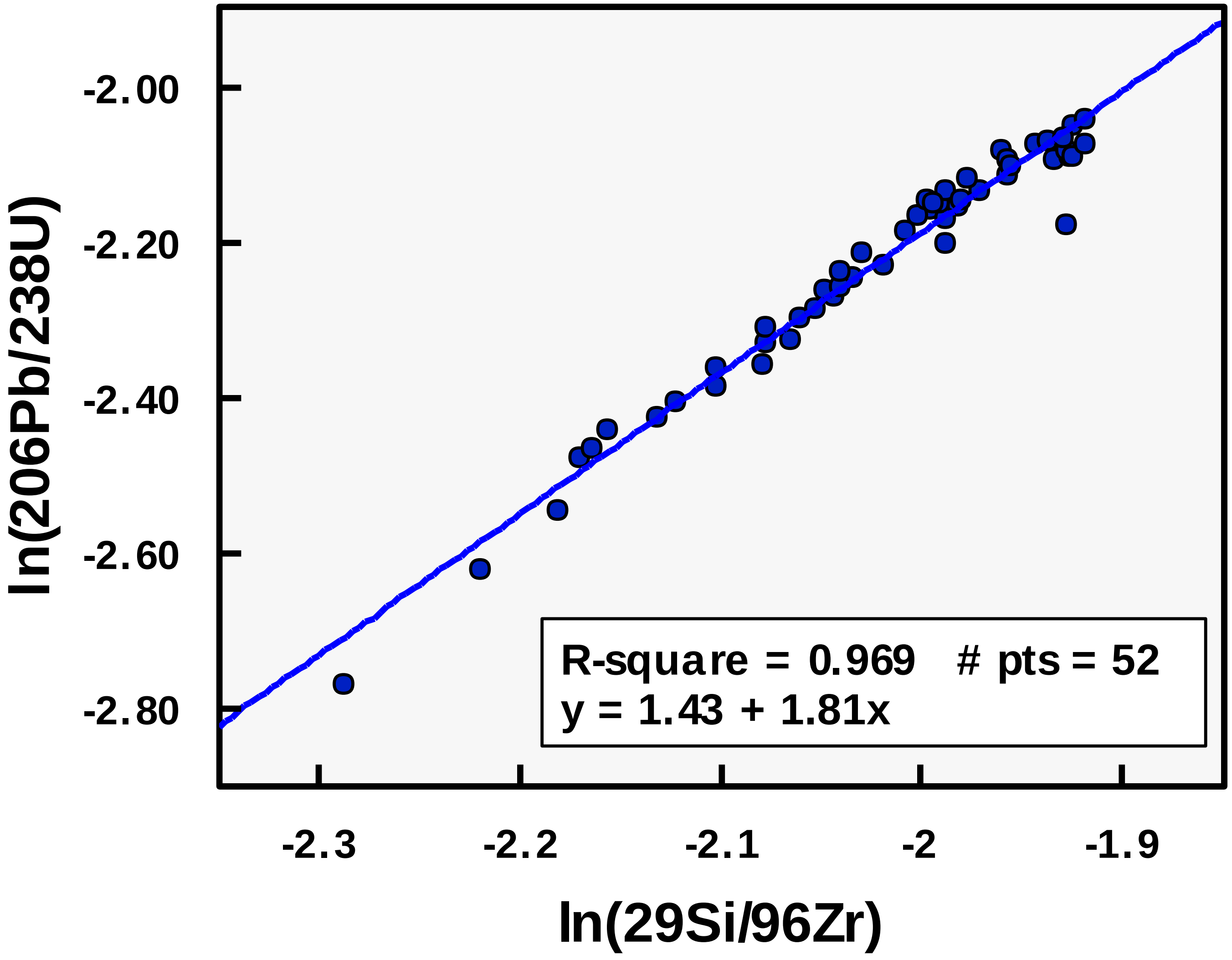
(Klotzli et al., 2009).



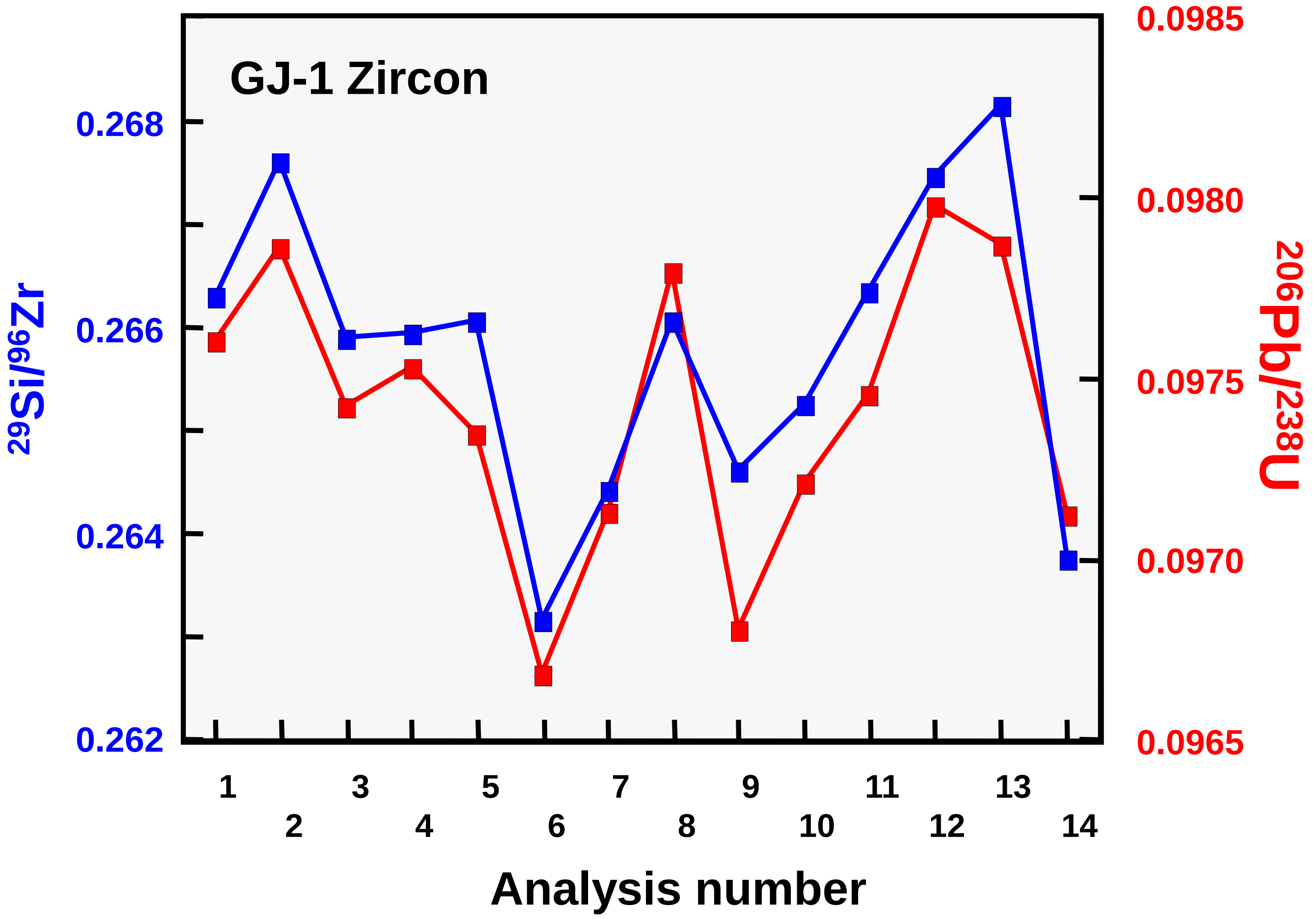
Gehrels et al., 2008

Down hole

$^{206}Pb/^{238}U$ vs. $^{29}Si/^{96}Zr$

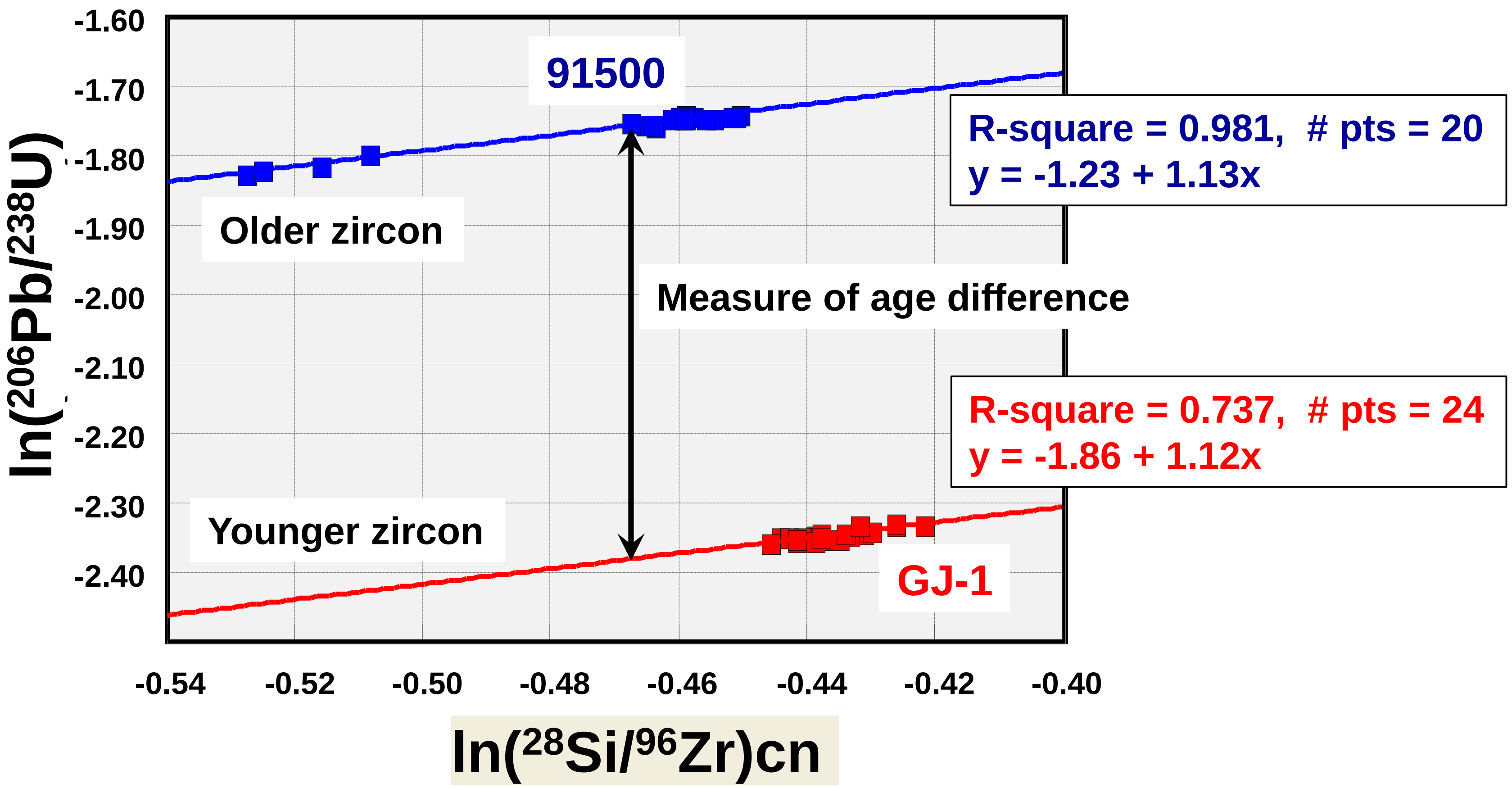


GJ-1 Zircon
Analyzed 14 times



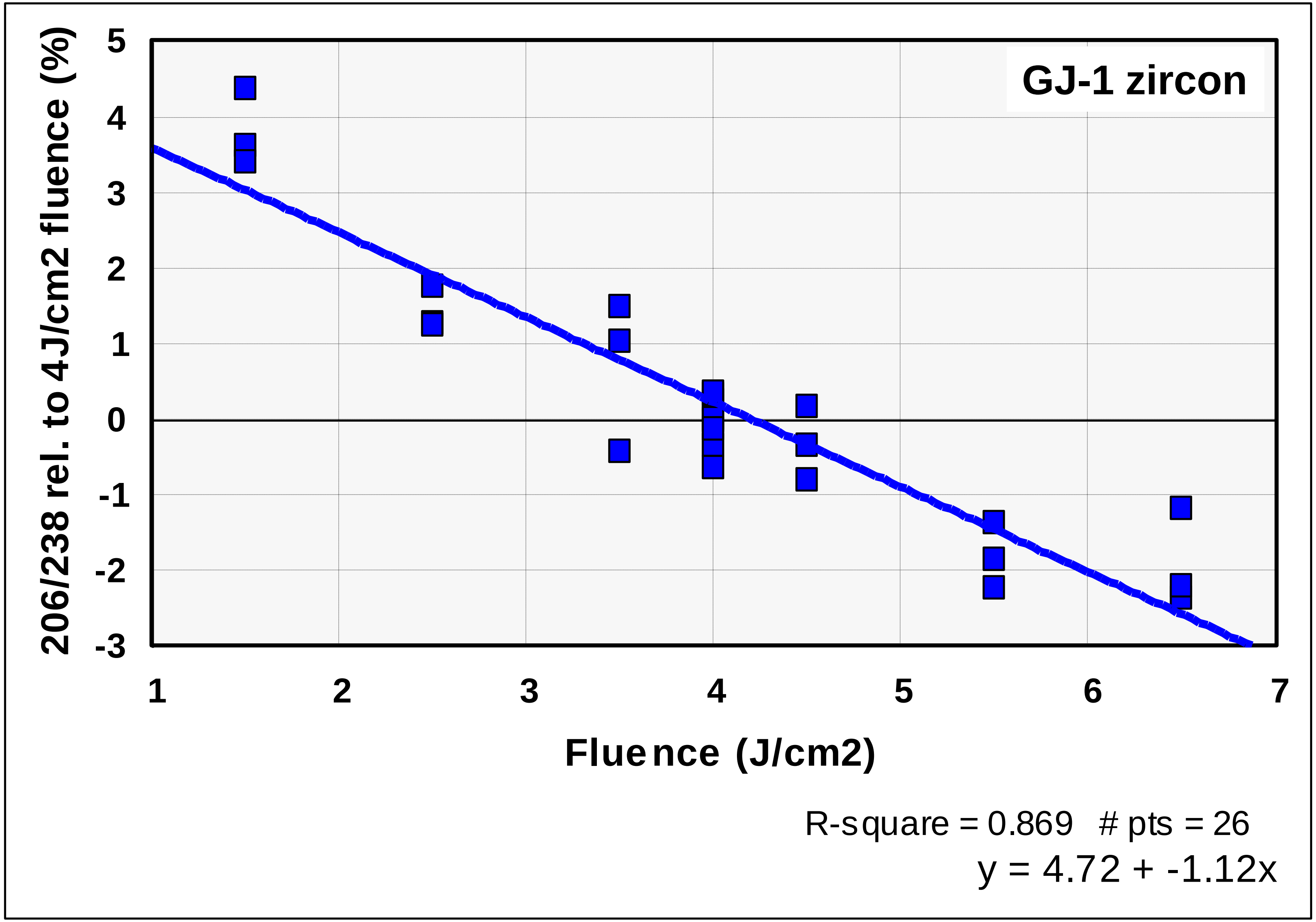
Calibration

$^{206}Pb/^{238}U$ vs. $^{28}Si/^{96}Zr$ Diagram

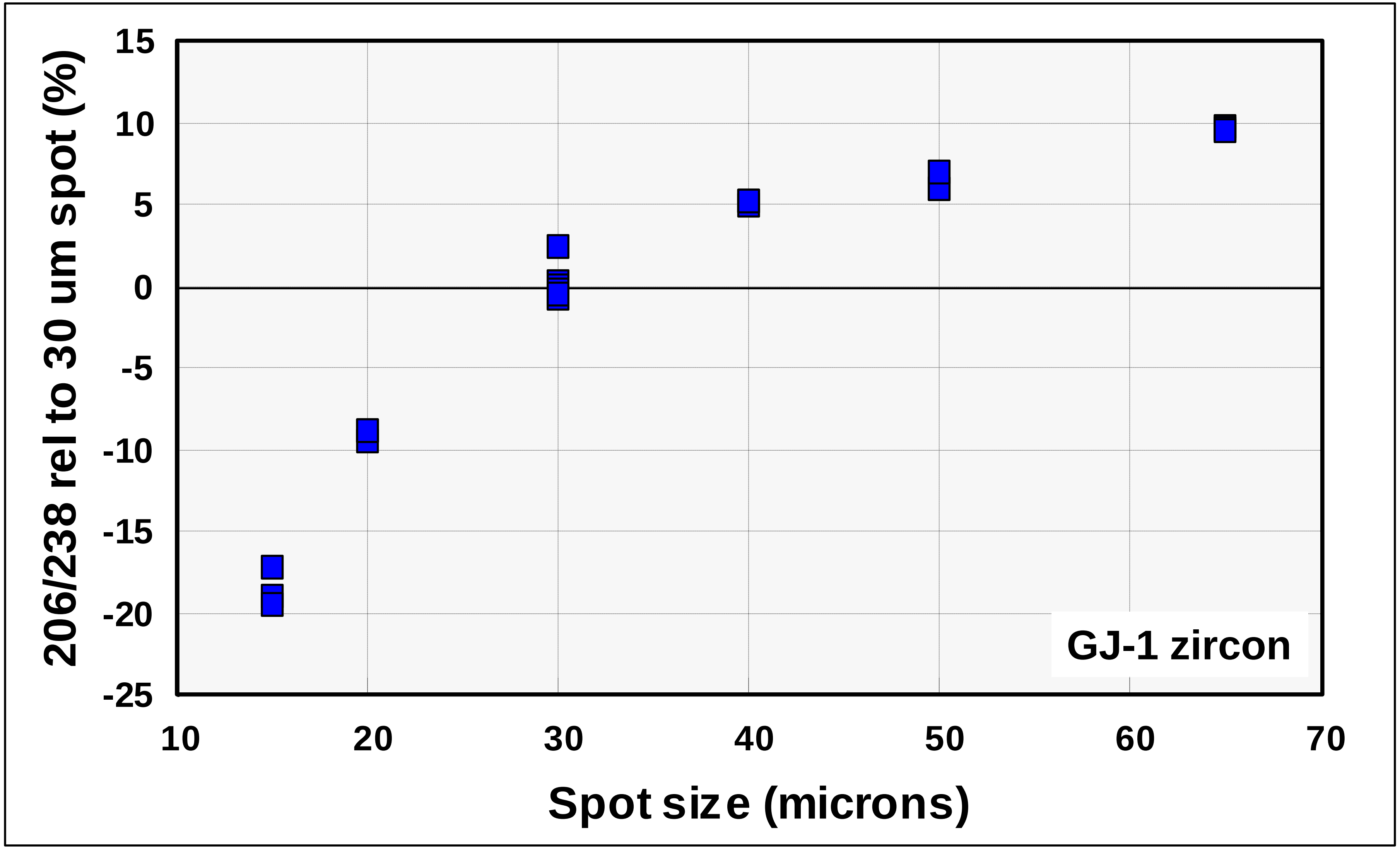


$(Pb_{sam}/U_{sam})_{corr} = (Pb_{sam}/U_{sam})_{meas} / (Si_{sam}/Zr_{sam})^{s}$ $\qquad$ $(Pb_{std}/U_{std}) = e^{i}$

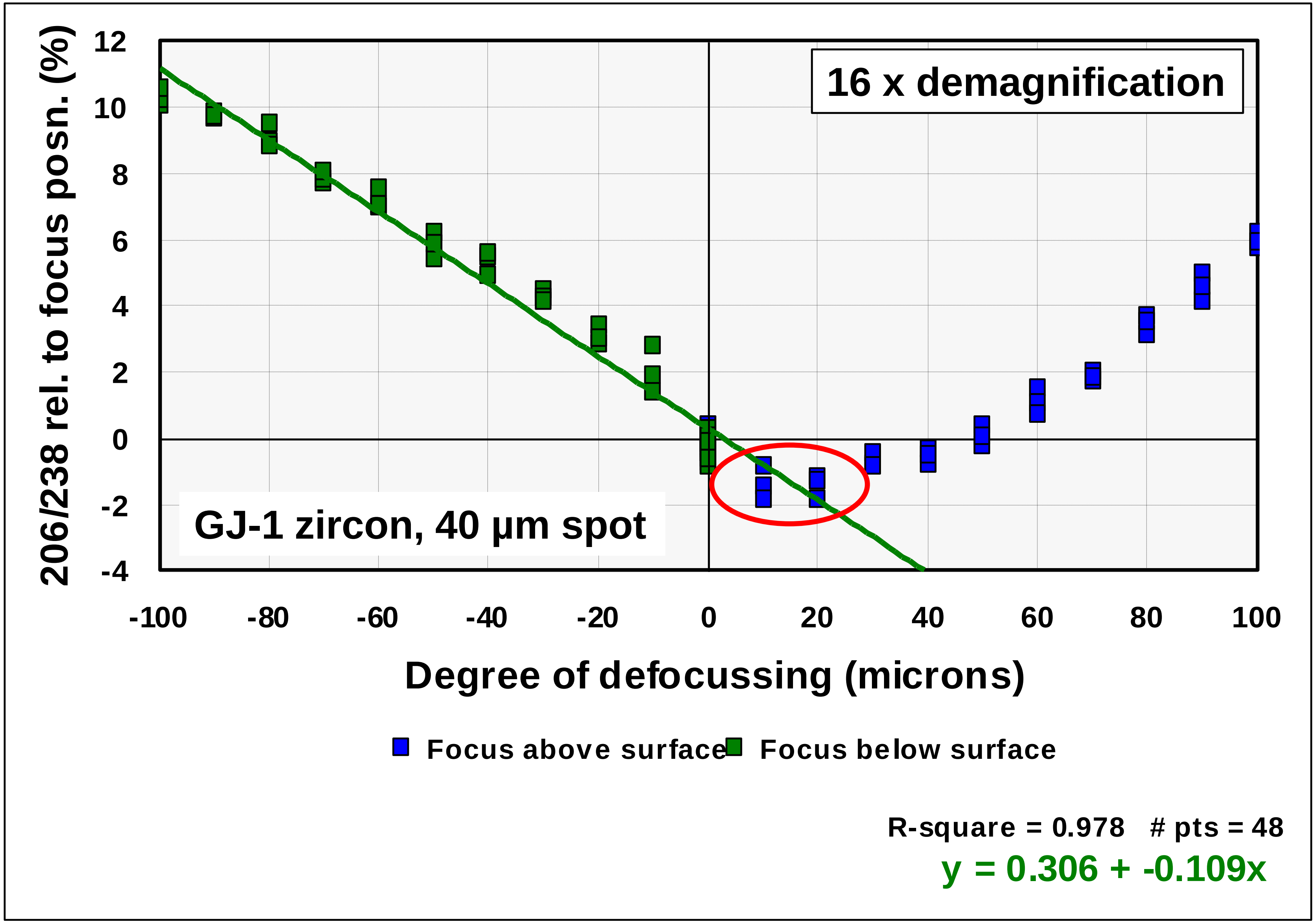
Effect of laser fluence on $^{206}Pb/^{238}U$ measurements



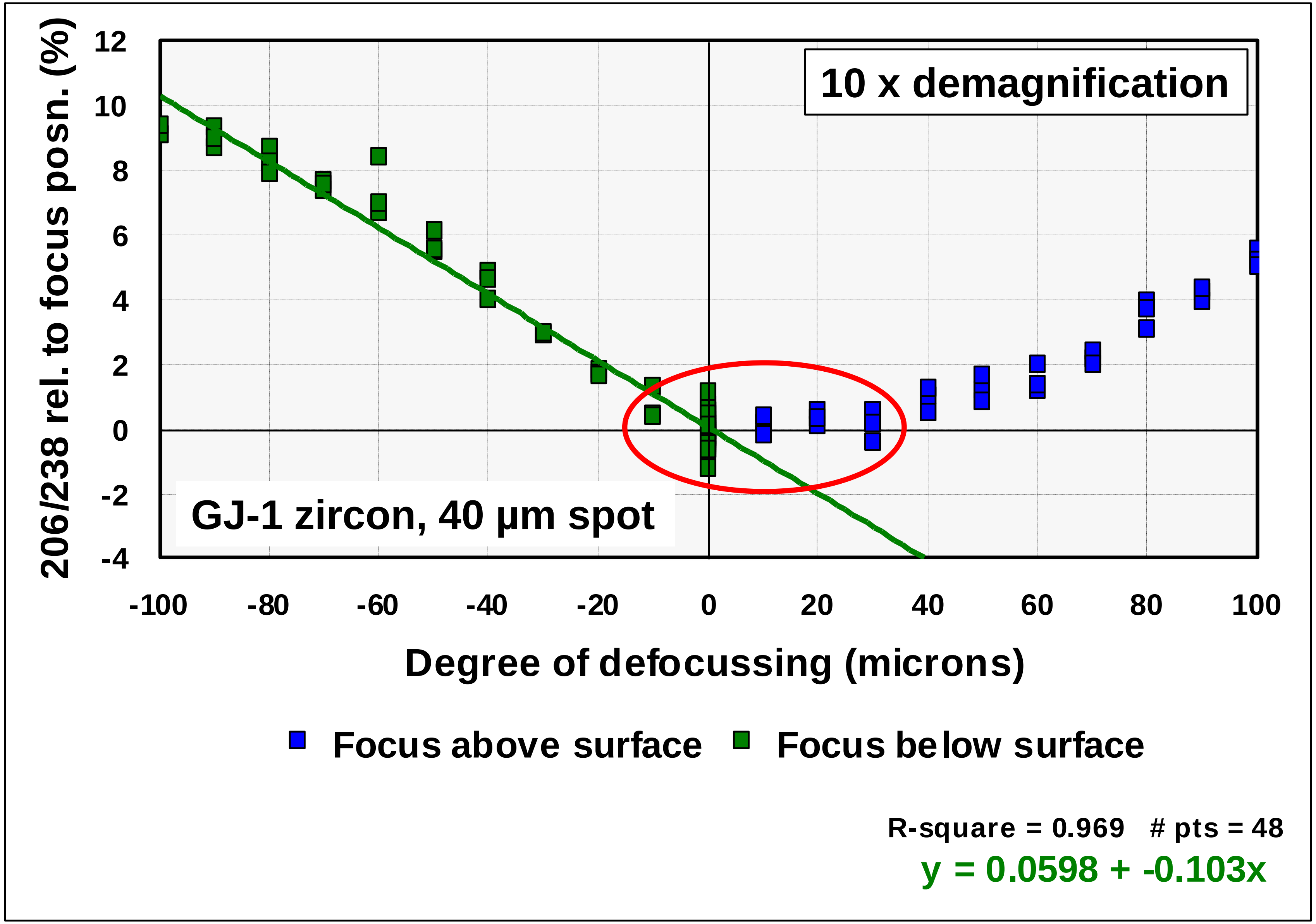
Effect of laser spot size on $^{206}Pb/^{238}U$ measurements



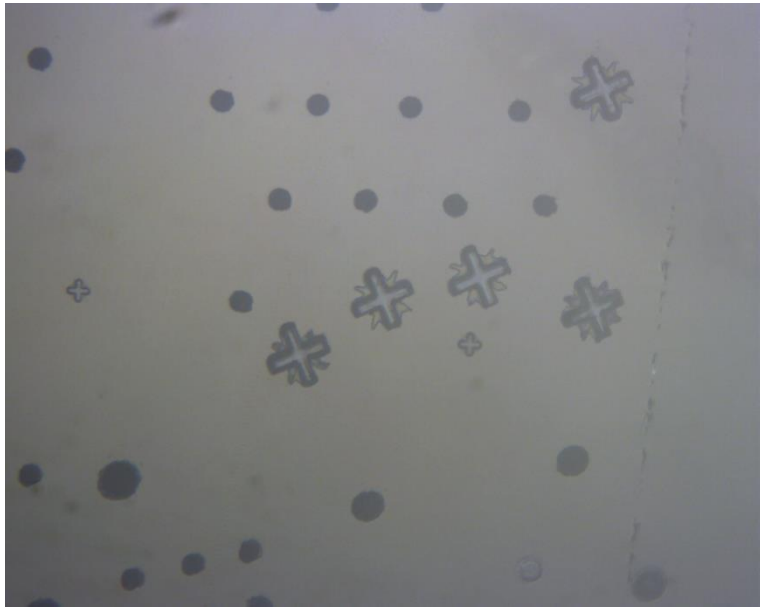
Effect of laser focus on $^{206}Pb/^{238}U$ measurements

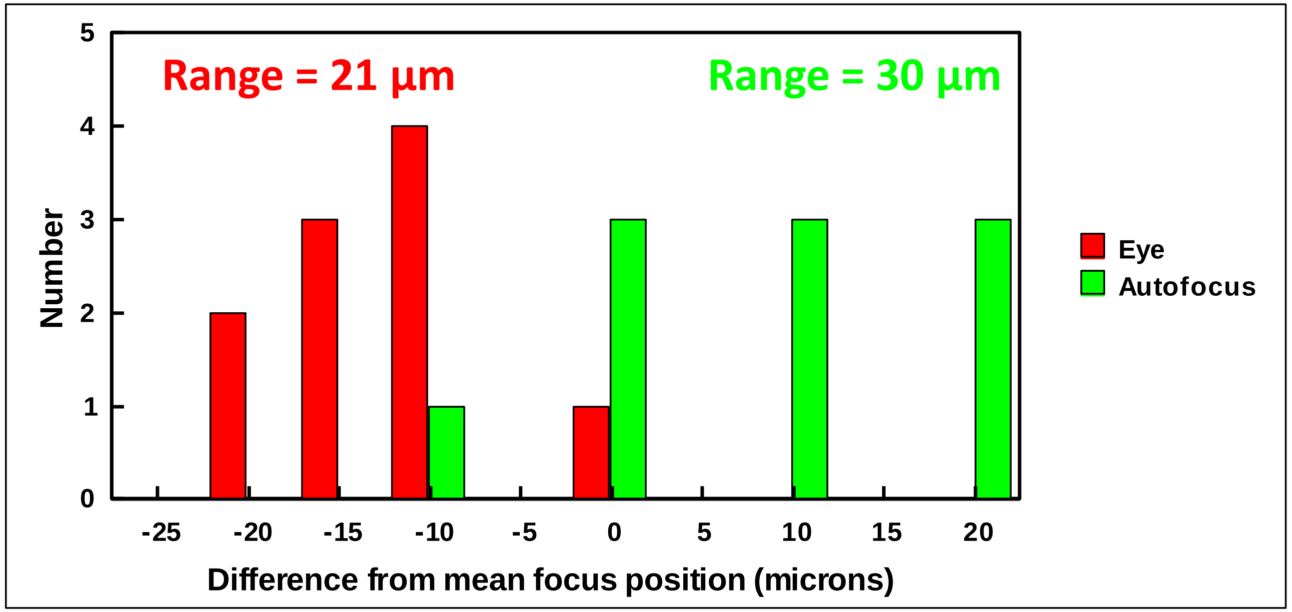


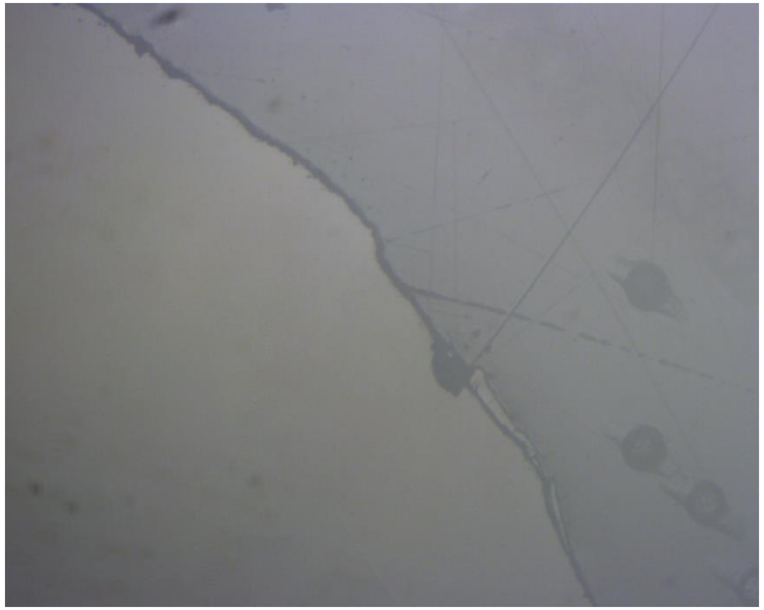
Effect of laser spot size on $^{206}Pb/^{238}U$ measurements

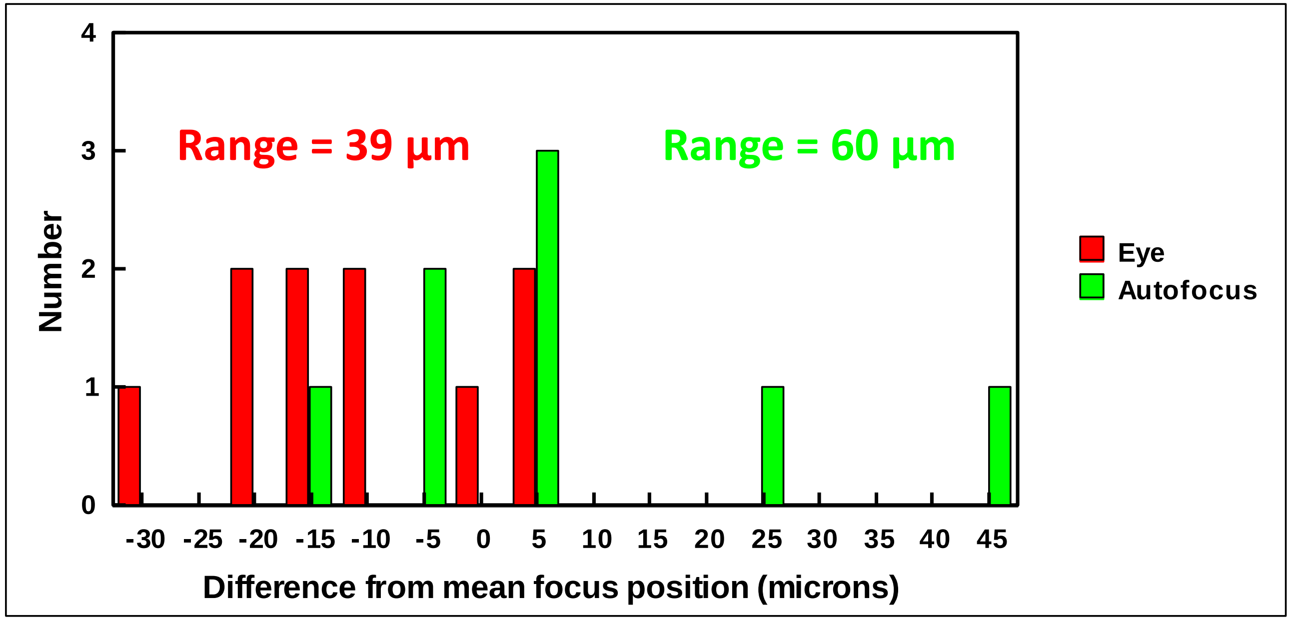


Focussing reproducibility





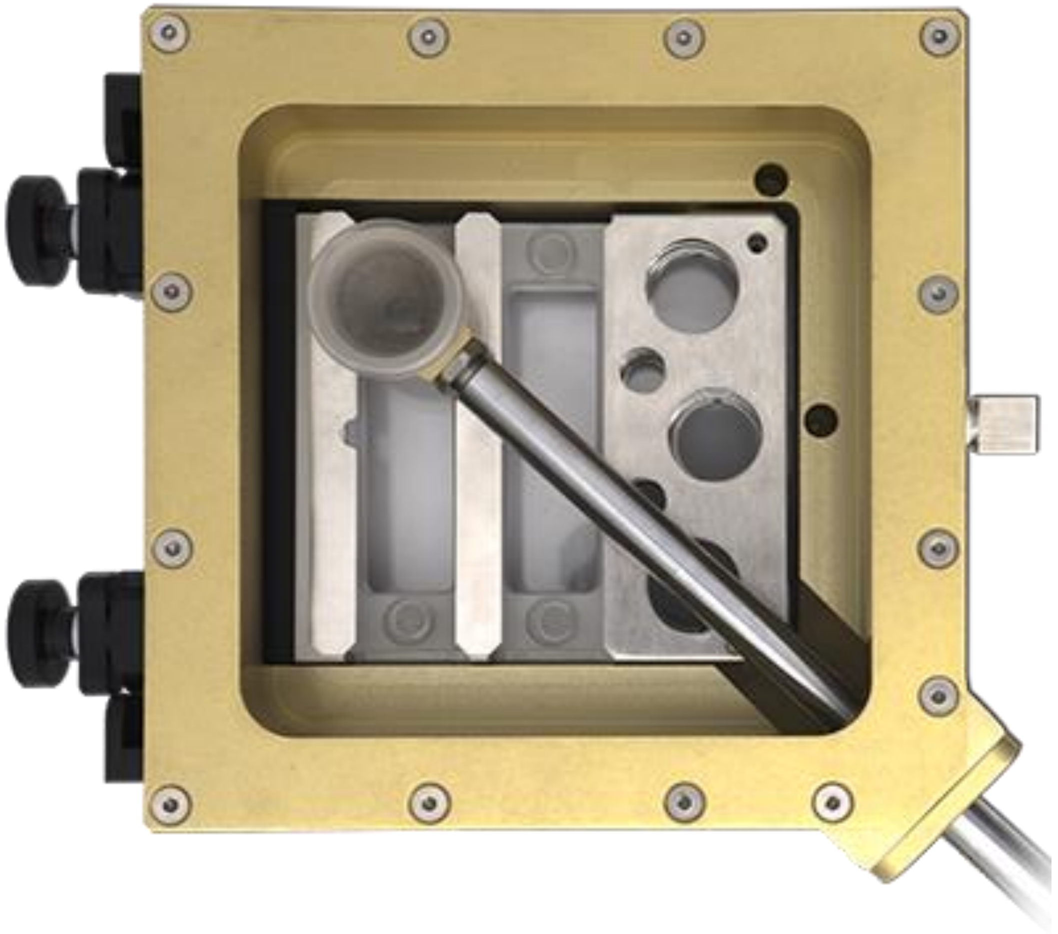


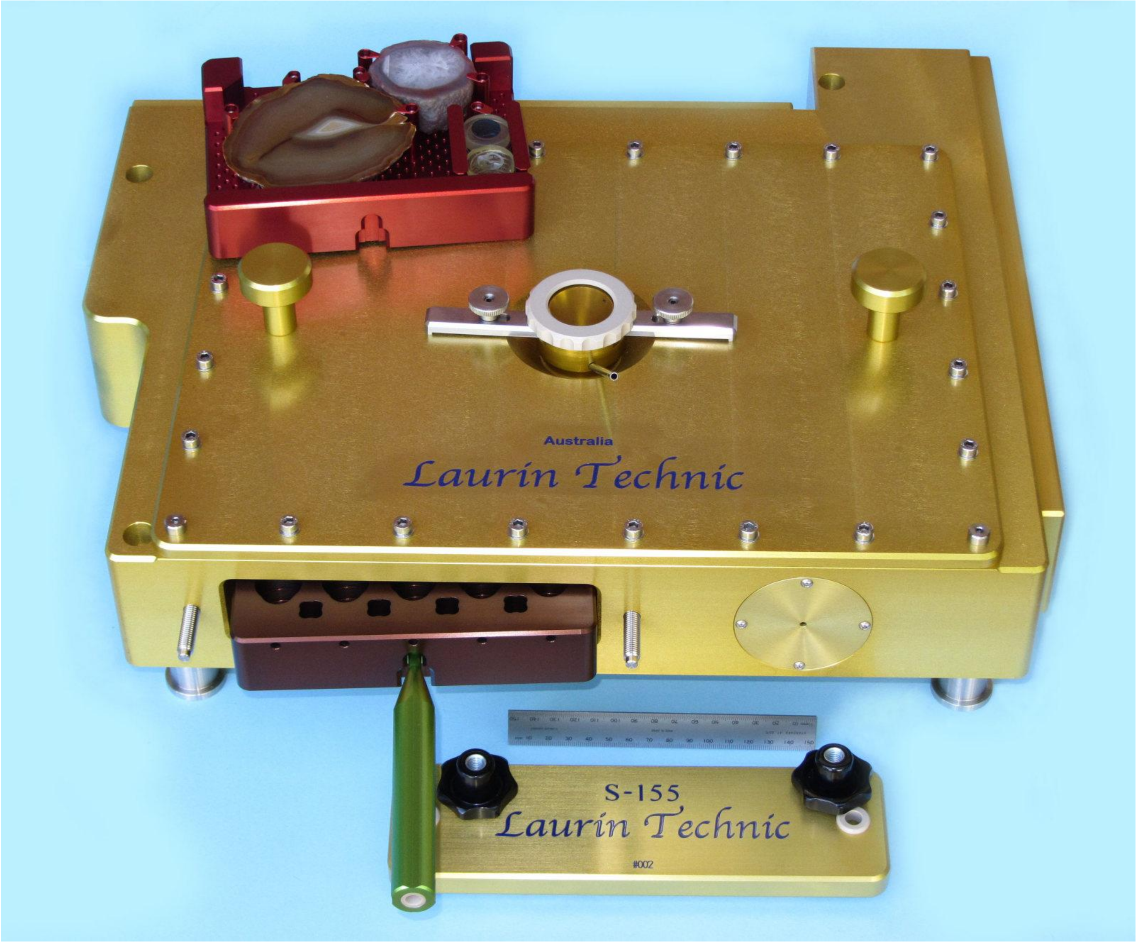


Solutions

- Use optical system with largest depth of laser focus;
- Mount samples and standards in same mount,
- Ensure perfect leveling of sample holder,
- Do not adjust focus between sample and standard

Effect of contaminant cell gases on Pb/U measurements





Effect of contaminant cell gases on Pb/U measurements

Kosler et al., JAAS, 2014

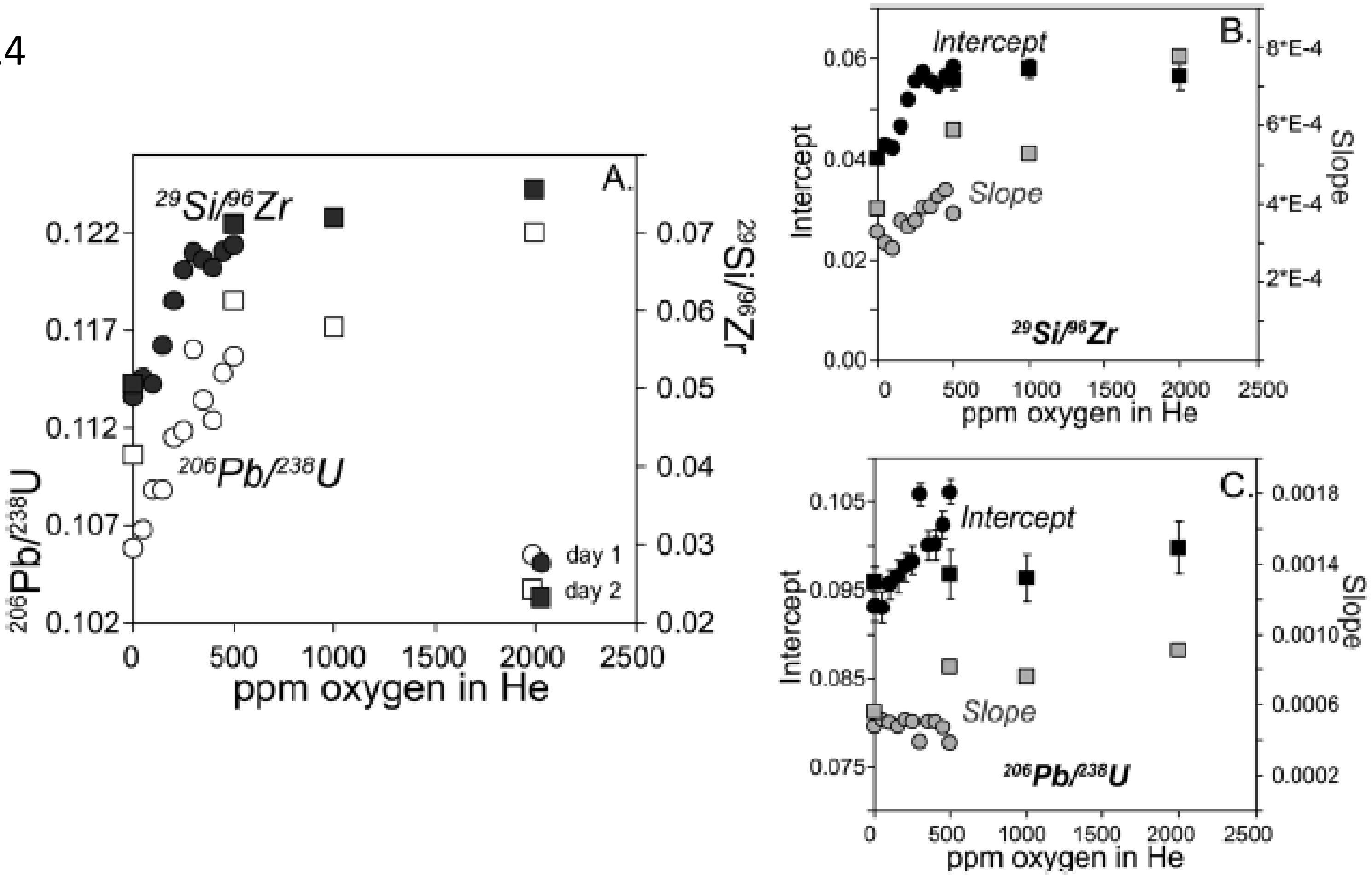
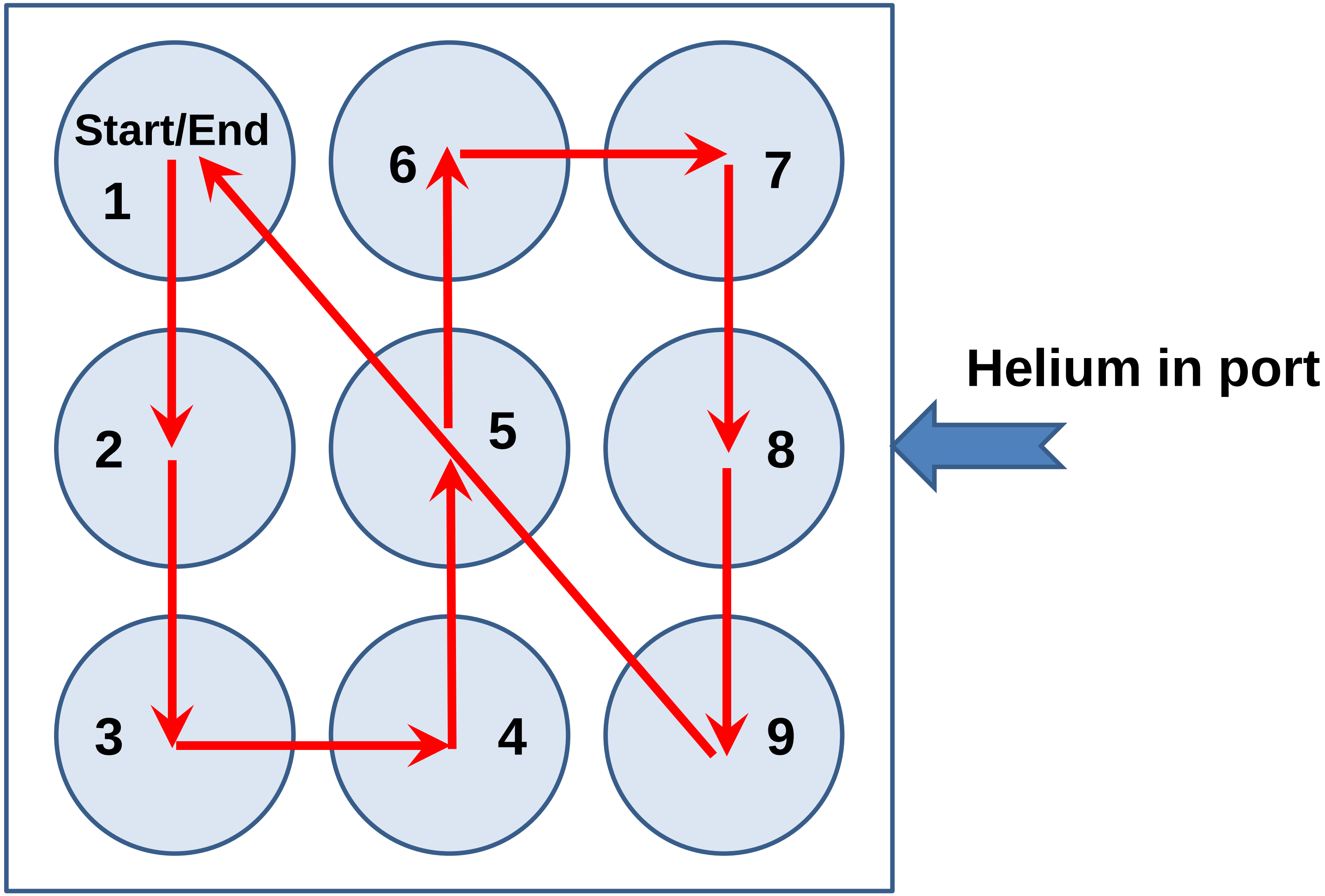
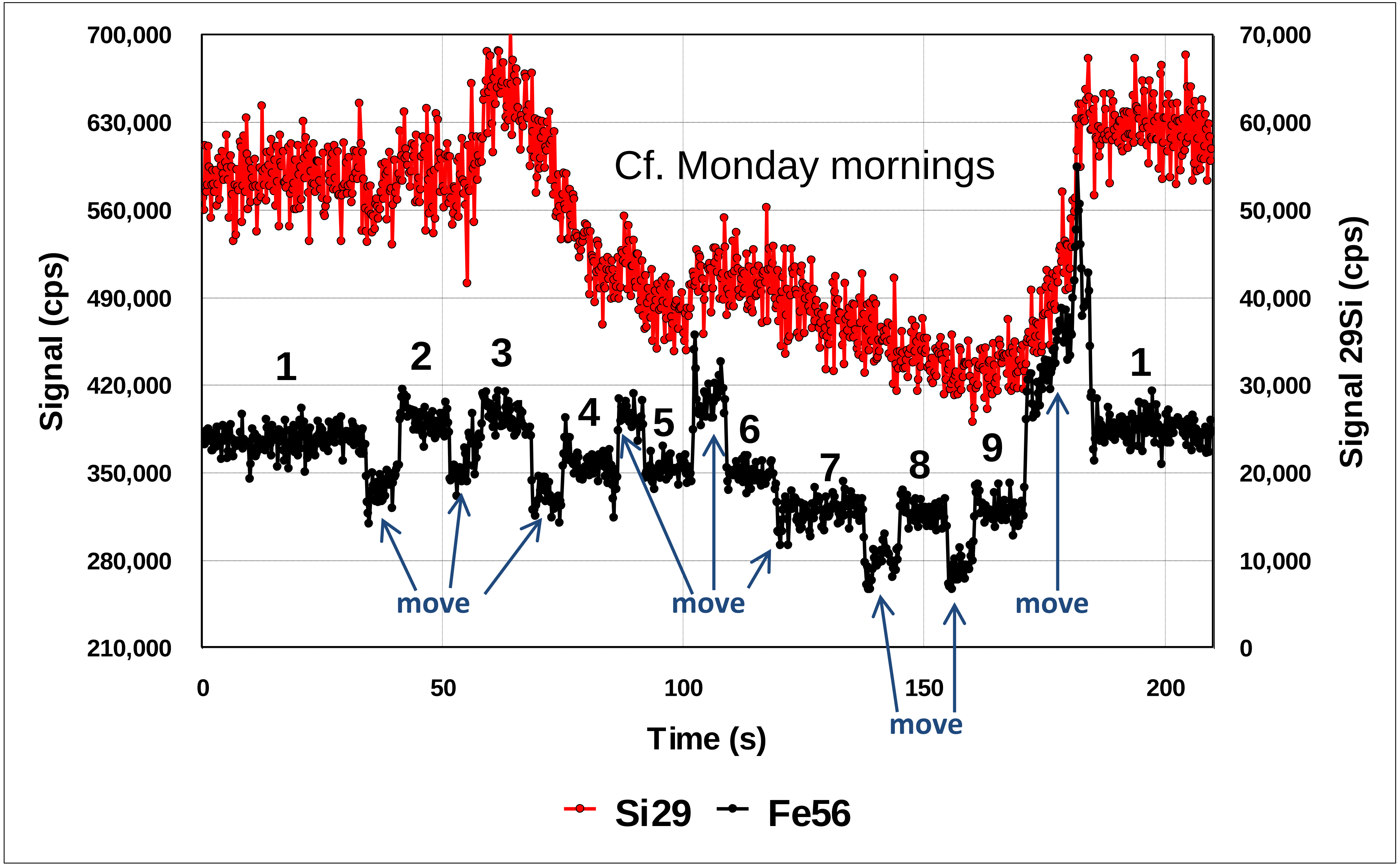


Fig. 4 The effects of oxygen in the He sample carrier gas on (A) the measured signal intensity ratios of $^{29}Si/^{96}Zr$ and $^{206}Pb/^{238}U$. Diagrams (B) and (C) show the separate effects of the oxygen concentration in the He sample carrier gas on the slope and the intercept[48] of the elemental fractionation trends of $^{29}Si/^{96}Zr$ and $^{206}Pb/^{238}U$, respectively. Uncertainties on the intercept values are 1 sigma.

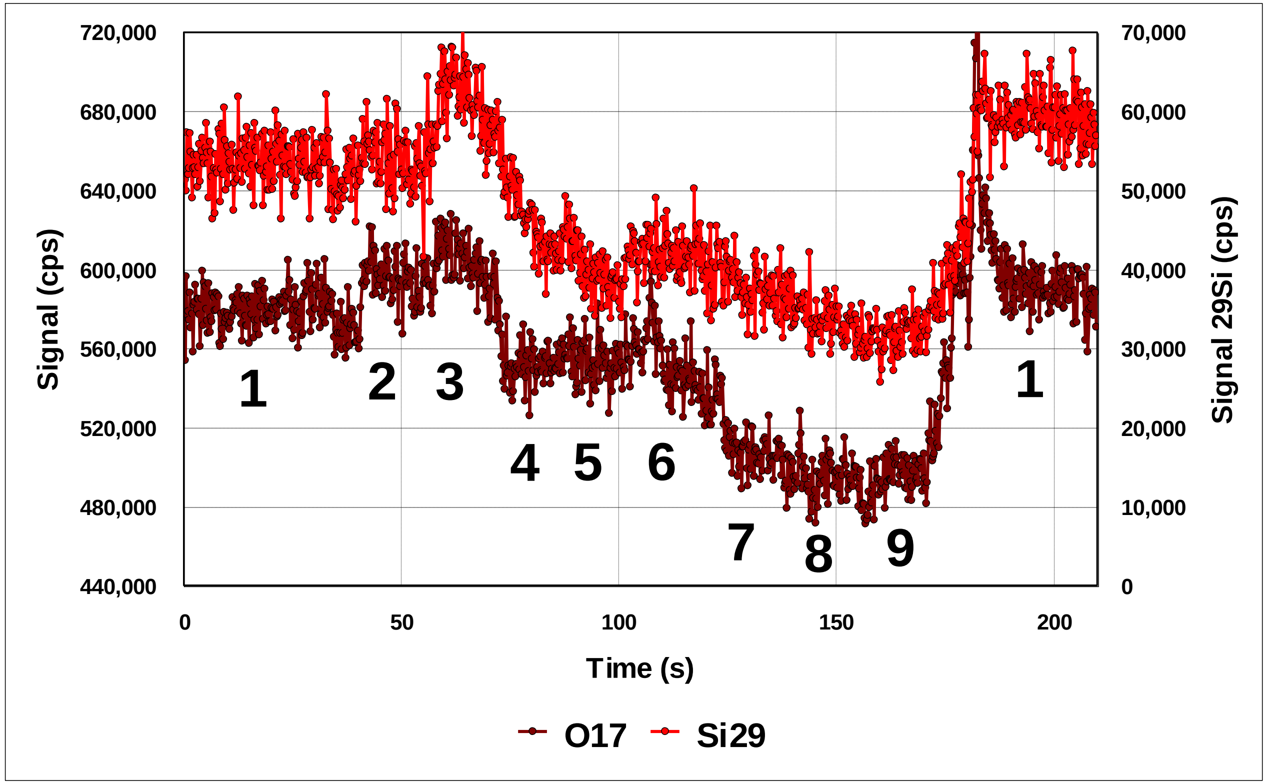
Stage movement sequence

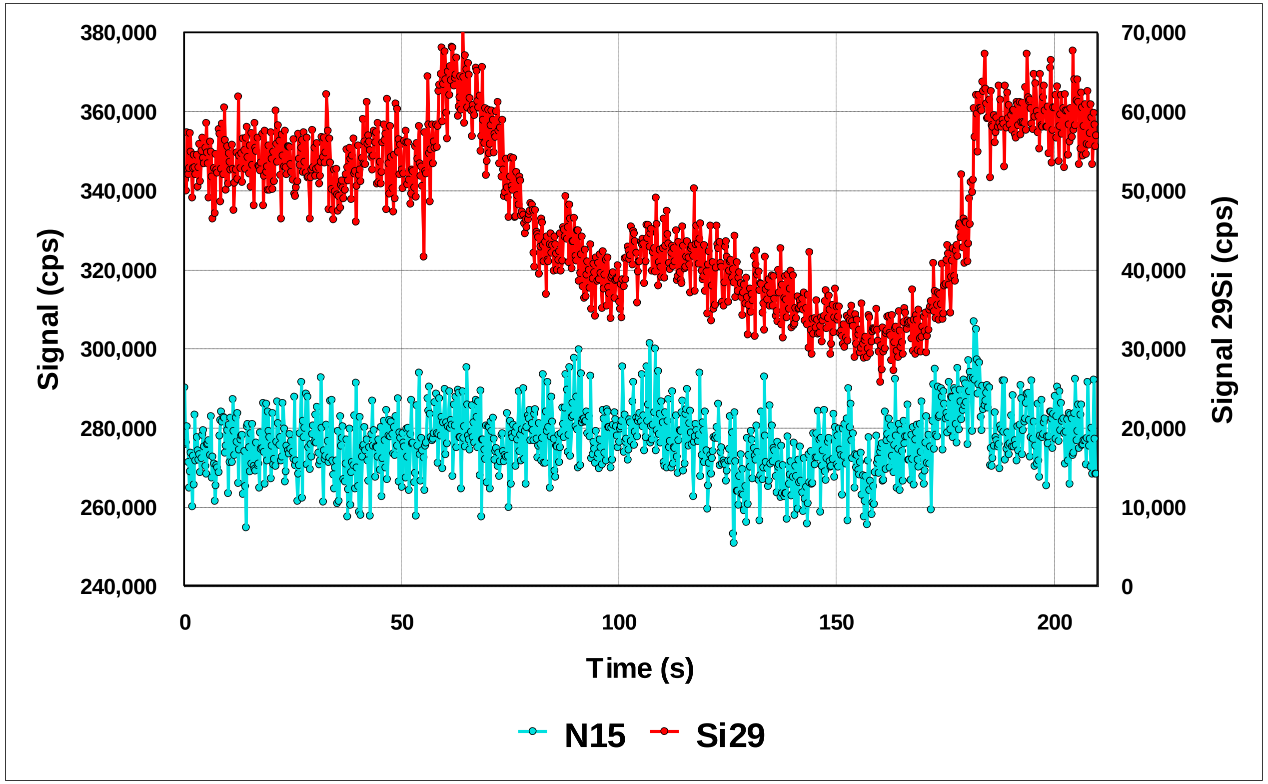


Effect of cup position on contaminant cell gases

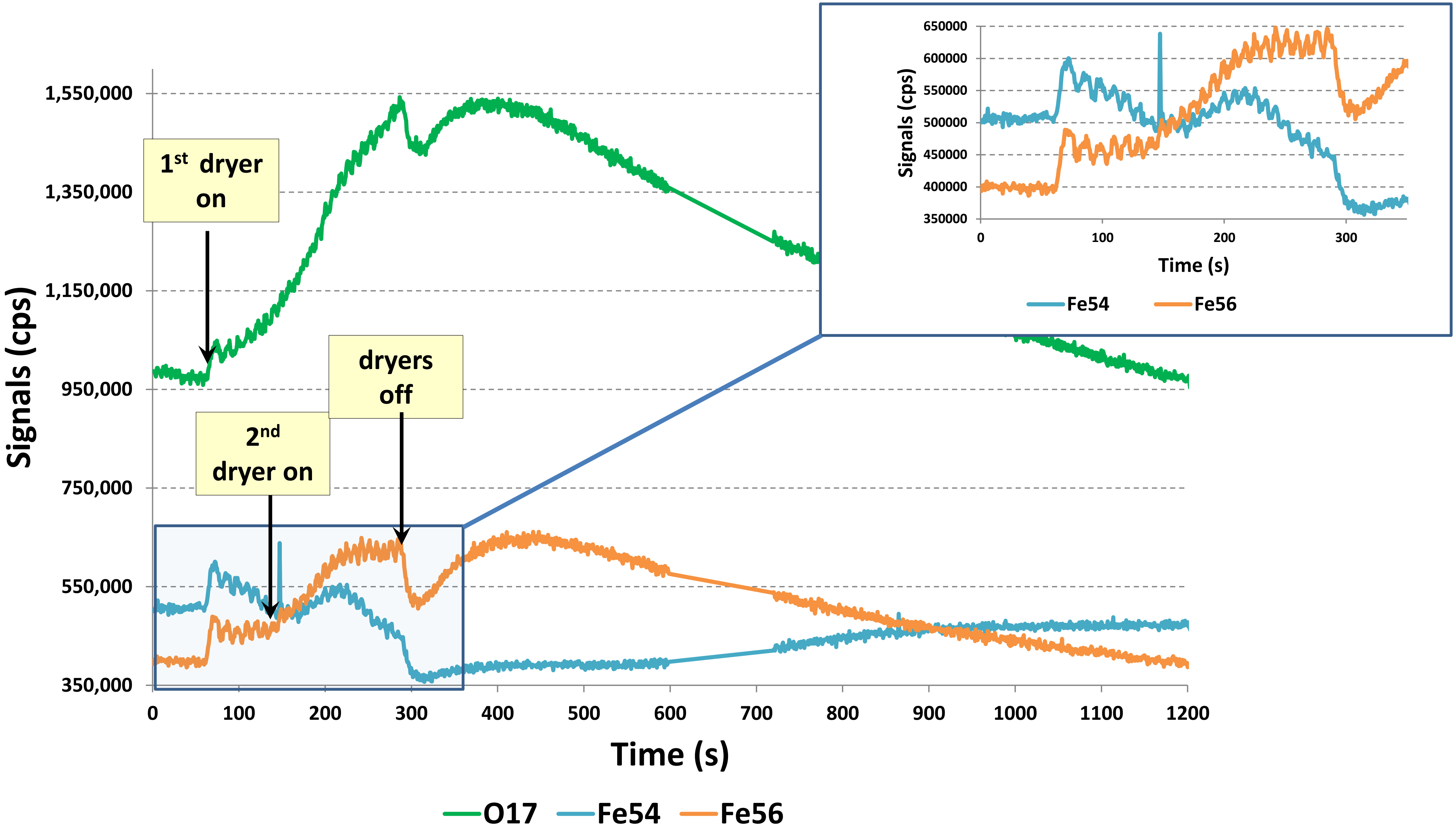


Effect of cup position on contaminant cell gases



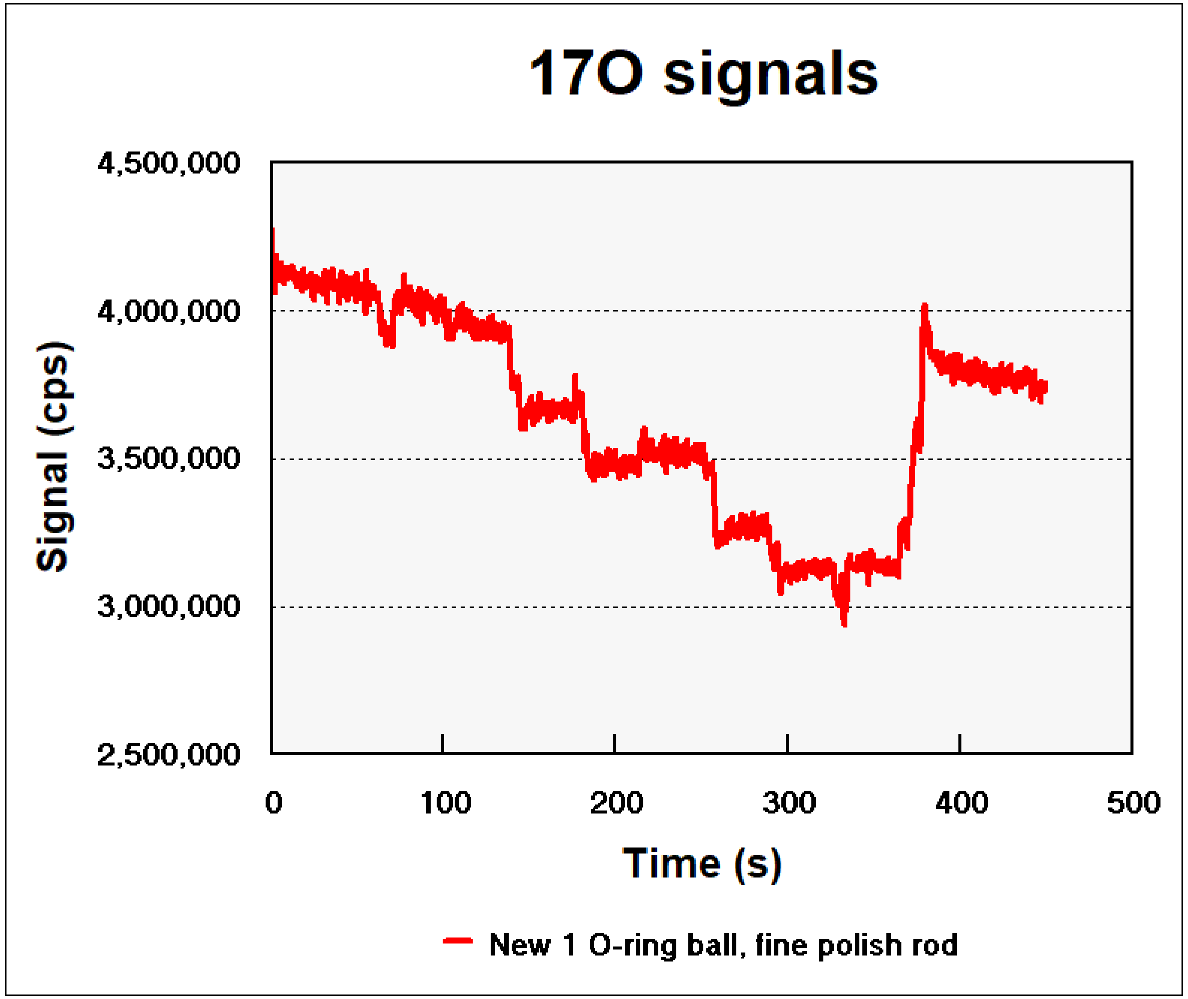


Effect of cell heating on contaminant cell gases

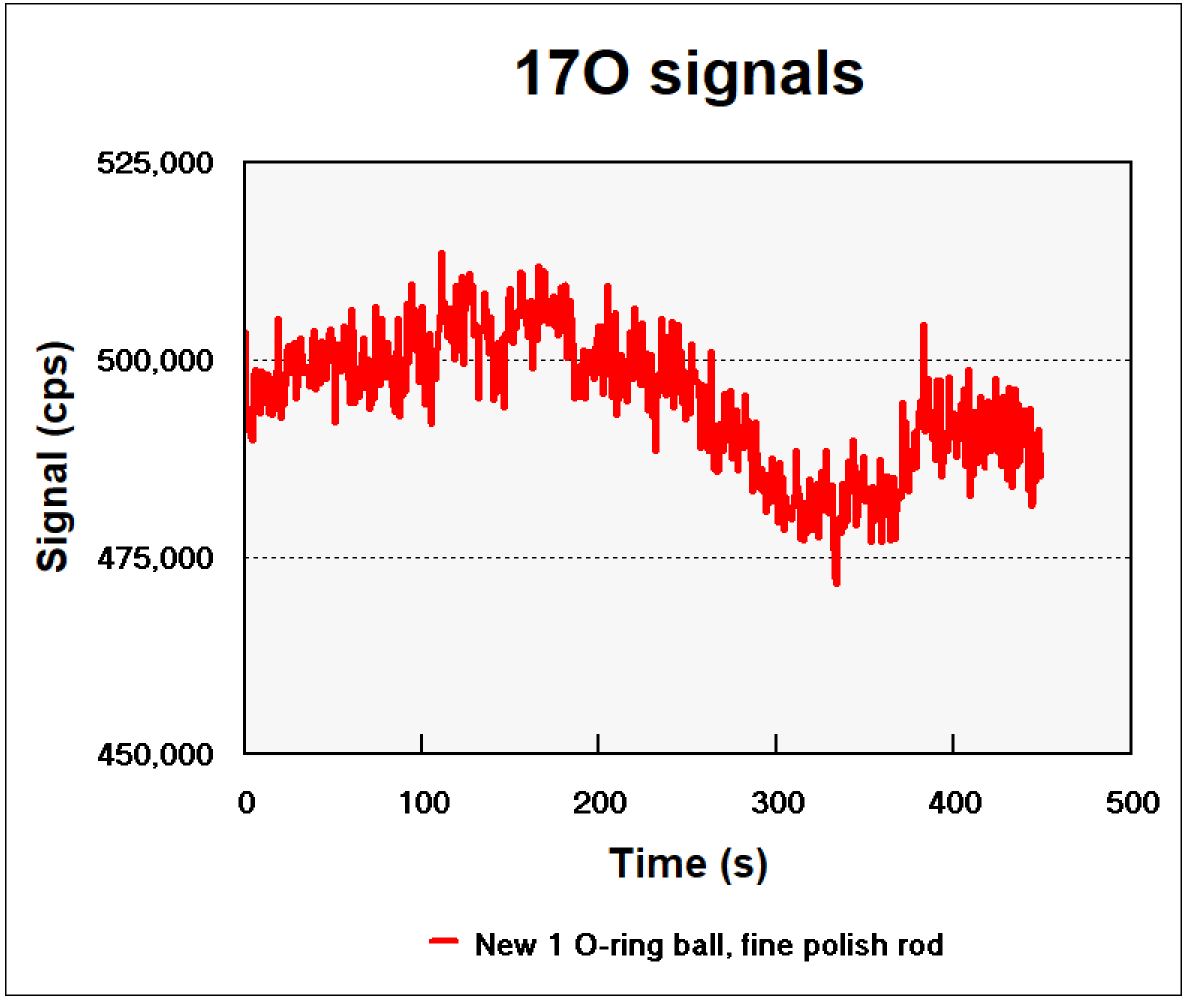


Effect of prolonged flushing on contaminant cell gases

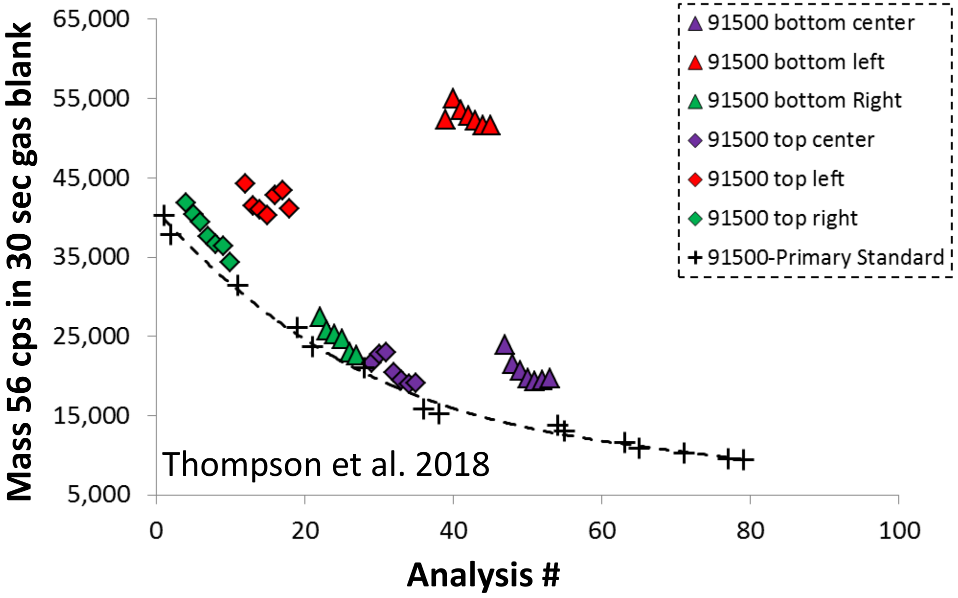
Instrument switched on for ca. 2 hours

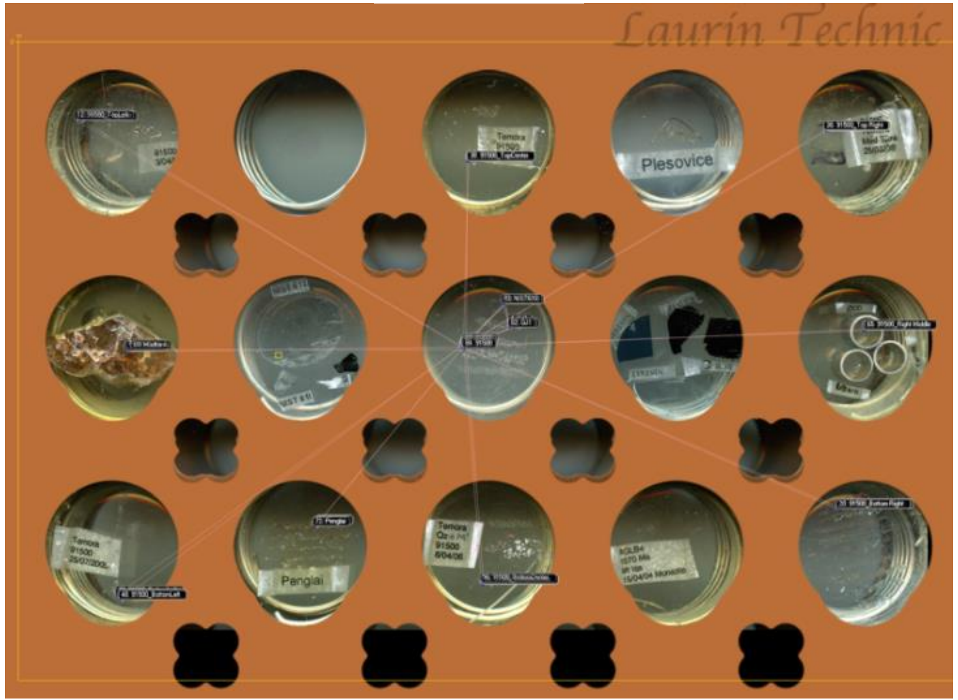


Instrument switched on for >24 hours



Influence of Atmospheric Air on U-Pb ages by LA-ICPMS

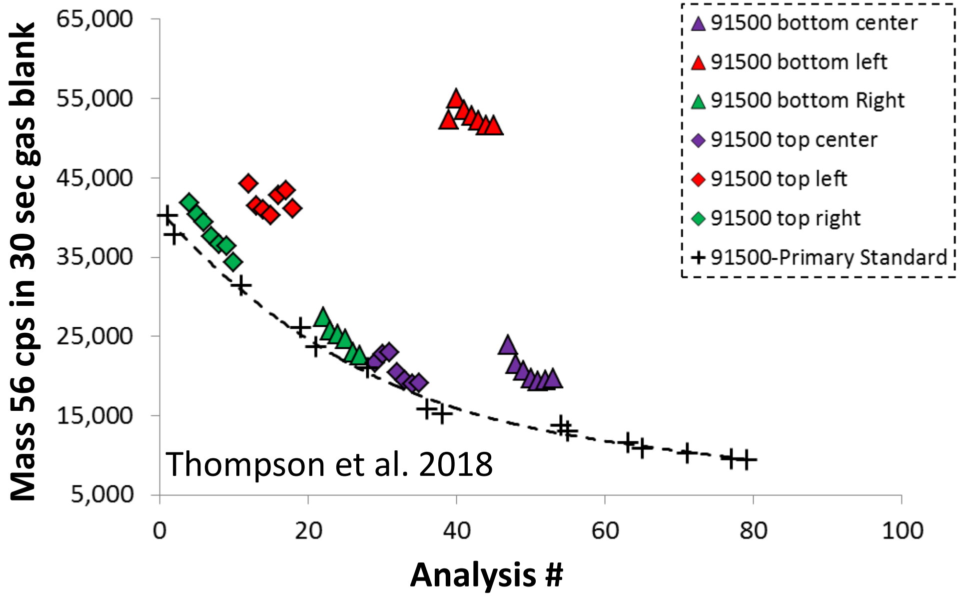


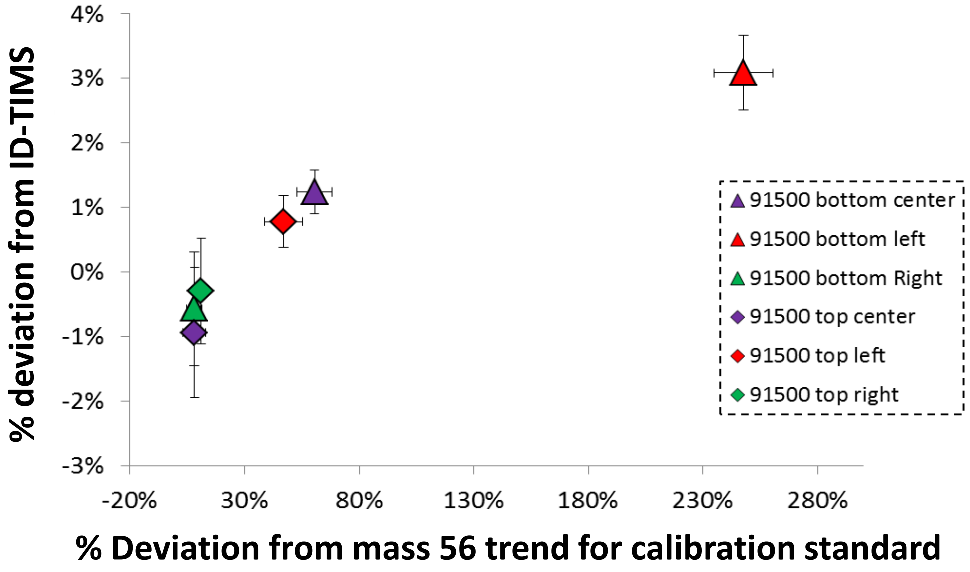


Experiment

- Variably degased epoxy mounts containing fragments of the 91500 zircon
- Atmospheric air quantified using mass 56 ($^{40}Ar + {}^{16}O$) in gas blank
- U-Pb ages quantified on the 91500 in the centre of the laser ablation cell
- Different locations in laser ablation cell have variable amounts of residual atmospheric air

Influence of Atmospheric Air on U-Pb ages by LA-ICPMS



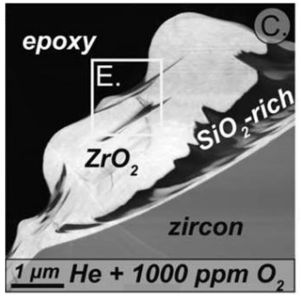


Results

- 91500 zircon measured in different locations show significant (4%) variance in U-Pb age
- Strong correlation with residual atmospheric air and measured U-Pb age

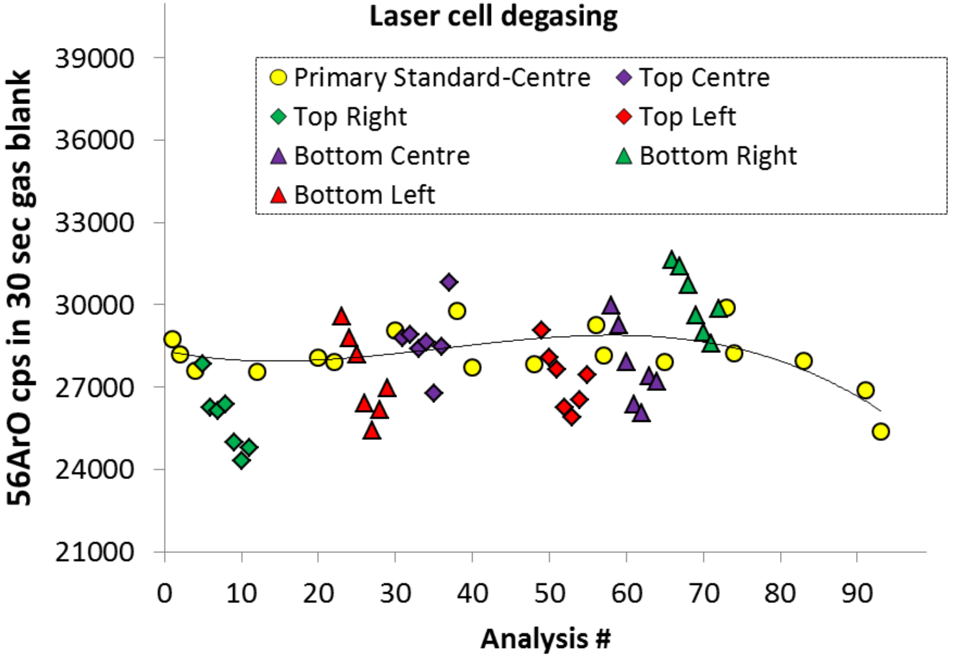
Interpretation

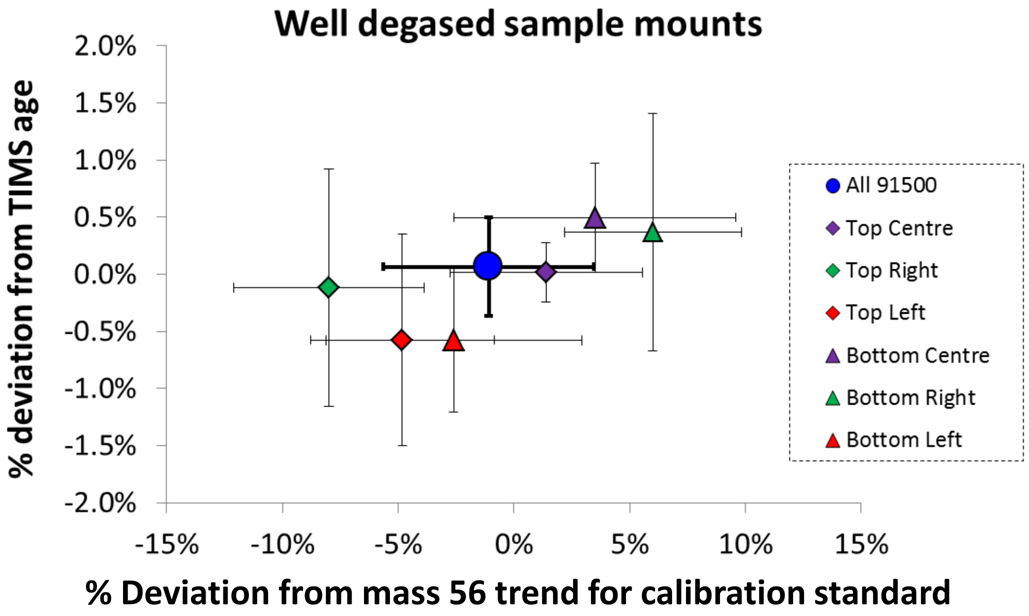
- Pb/U fractionation increases in the presence of O_2 (Kosler et al. 2014) giving older U-Pb ages
- Trace atmospheric air changes the relative ionization in the ICP – similar to diatomic gas addition (Durrant 1994, Kosler et al. 2014)



Kosler et al. 2014 – JAAS 29, p832

Influence of Atmospheric Air on U-Pb ages by LA-ICPMS





- **Repeat of experiment after degasing all mounts >24 hours in a desiccator under vacuum**
- **No systematic variation in mass 56**
- **No bias seen in U-Pb ages regardless of position in laser ablation cell**
- **Prerequisite: need homogenous gas flows throughout laser cell!**

Weighted mean of 91500 in 6 locations in laser cell:
Mean = 1063.2±4.5 [0.43%] 95% conf.
Wtd by data-pt errs only, 0 of 6 rej.
MSWD = 0.86, probability = 0.53

Desiccator

Vacuum pump

Some initial testing back in 2012 on the S-155 large format laser cell

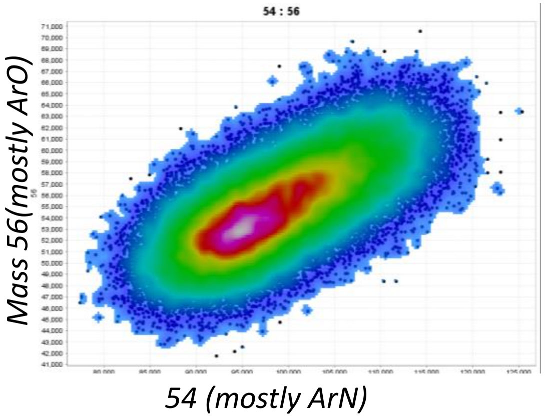
- We mapped the signal intensity of several masses affected by atmospheric air (e.g. m/z 56) across our laser cell – the holder at the time could fit 15 1” rounds (currently used holder can fit 20).

- These tests were done before we had optimized the sample exchange procedure and show how residual atmospheric air can present itself in the laser cell

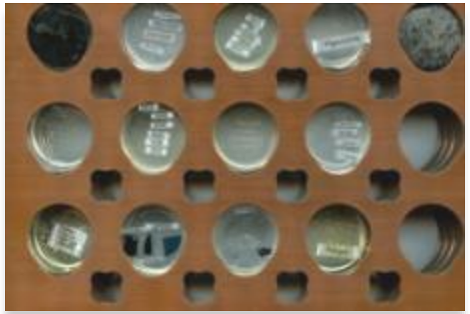
- We have since changed the sample exchange procedure and a few other things to minimize the total amount and variations within the cell of atmospheric air

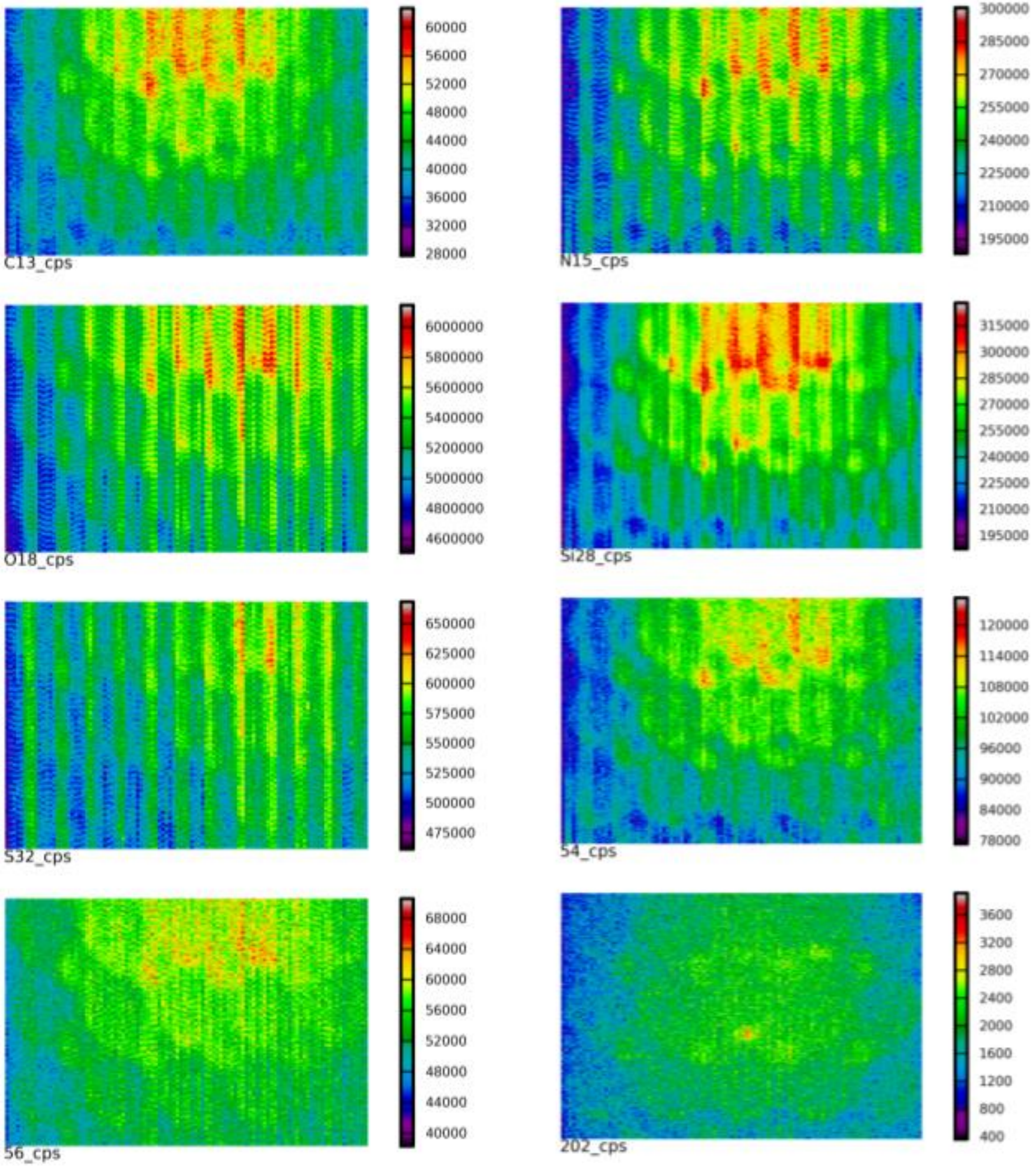
Mapping of air (laser off)

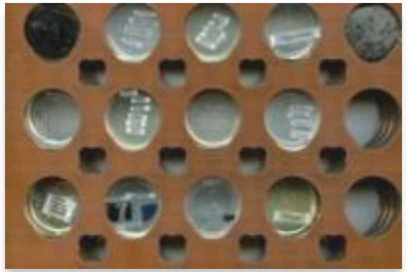
correlation
Between all masses
Except Hg

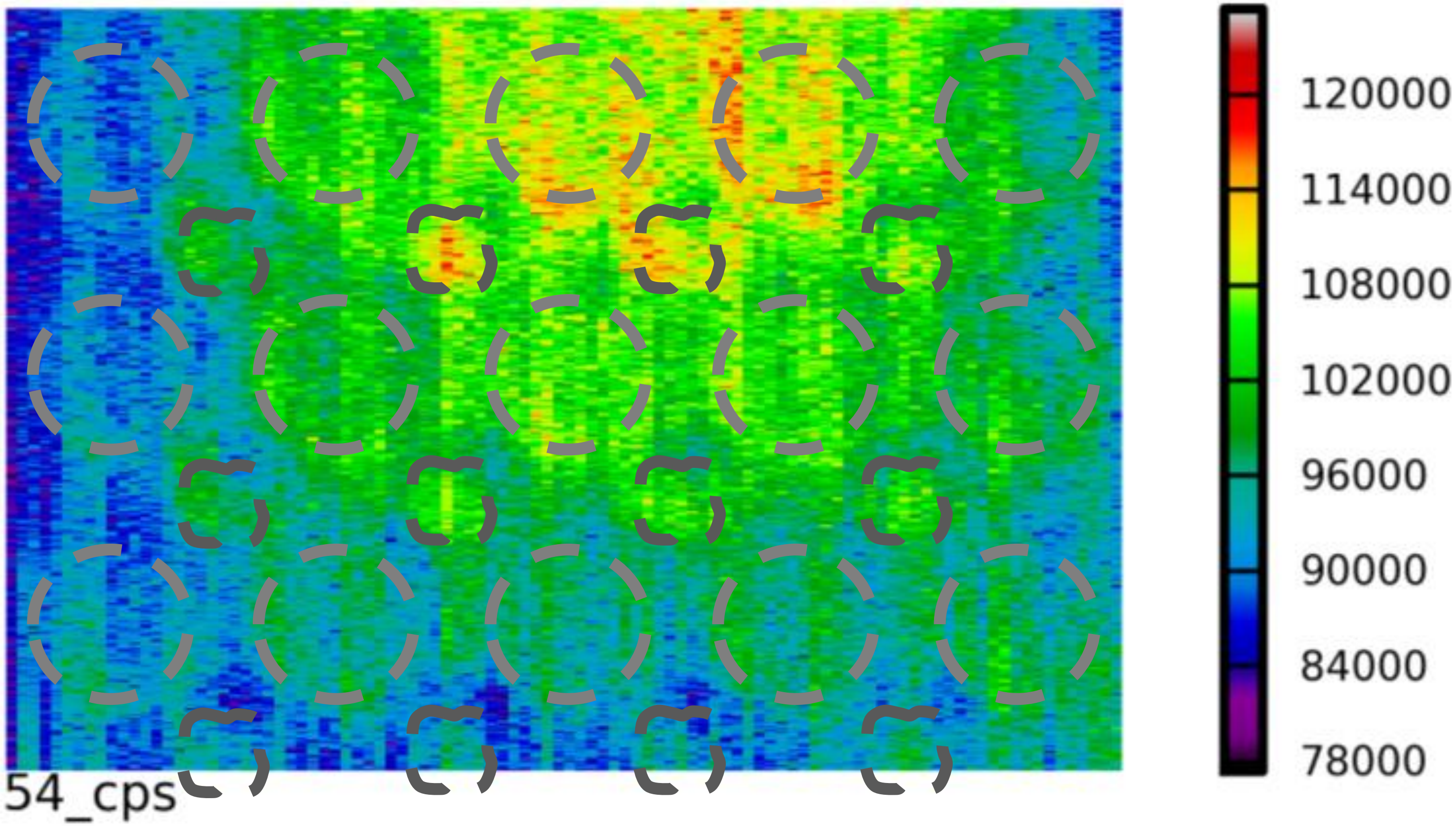


Harmonic artefacts
(prob. Unrelated to cell)

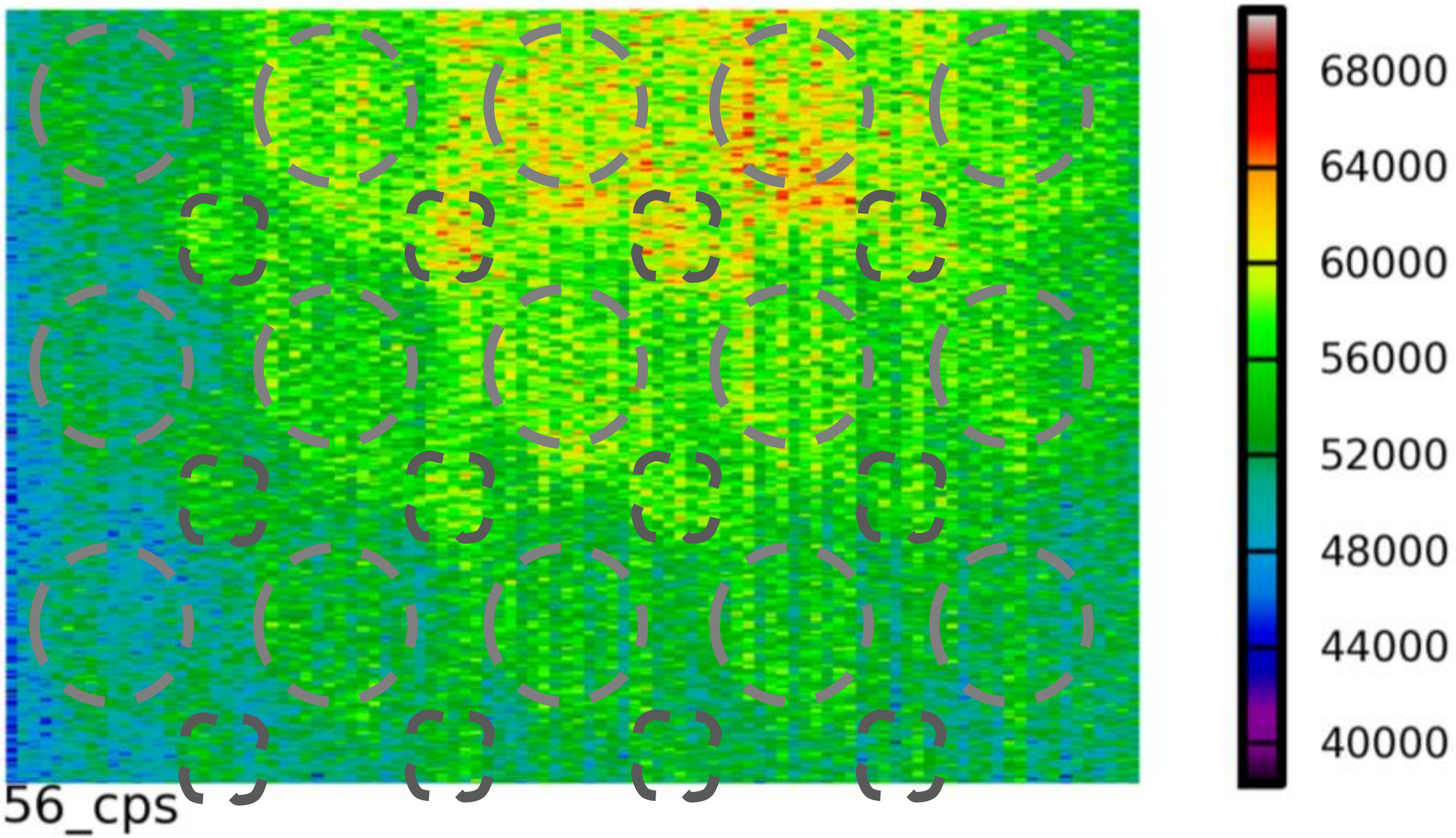


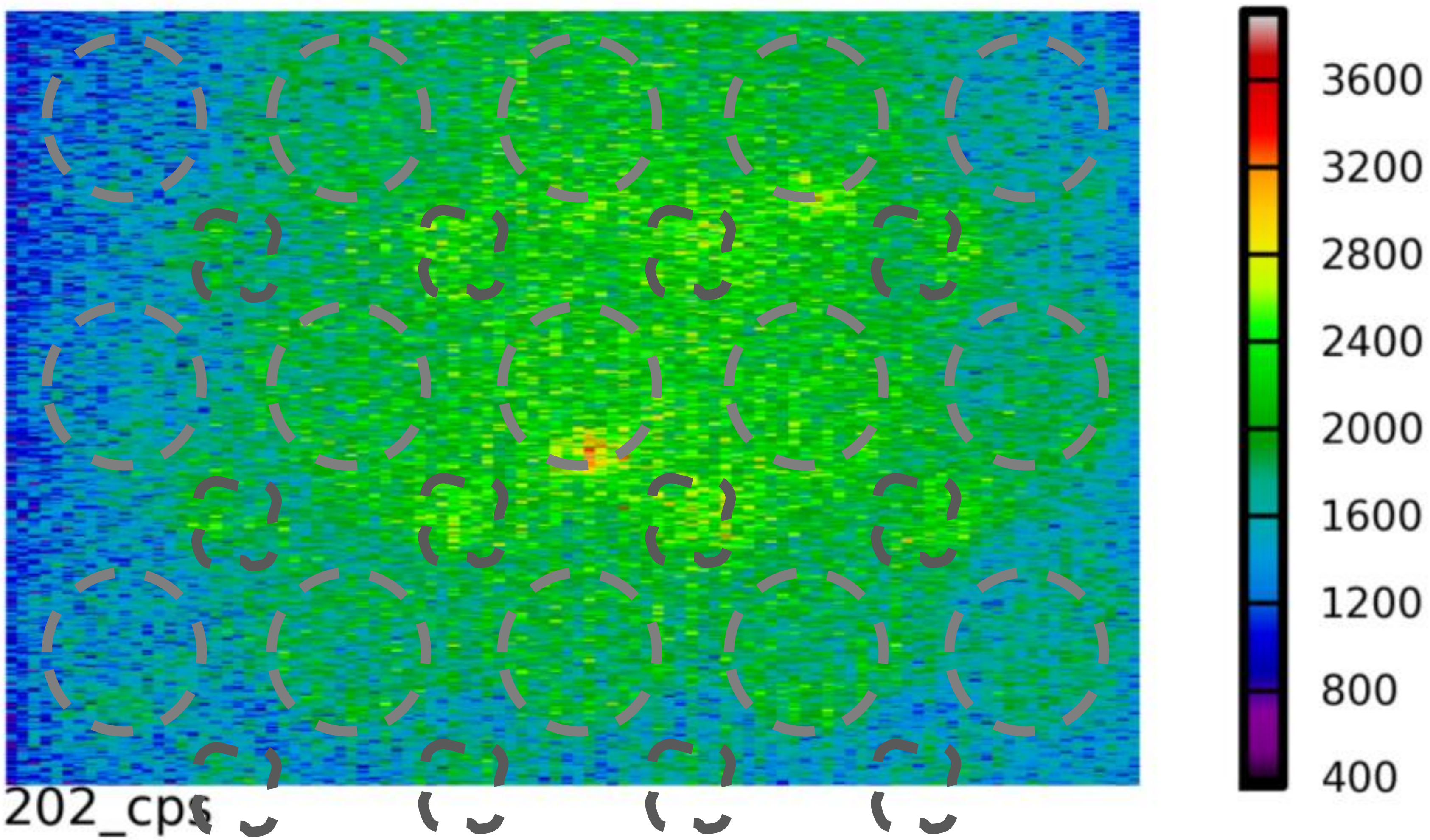






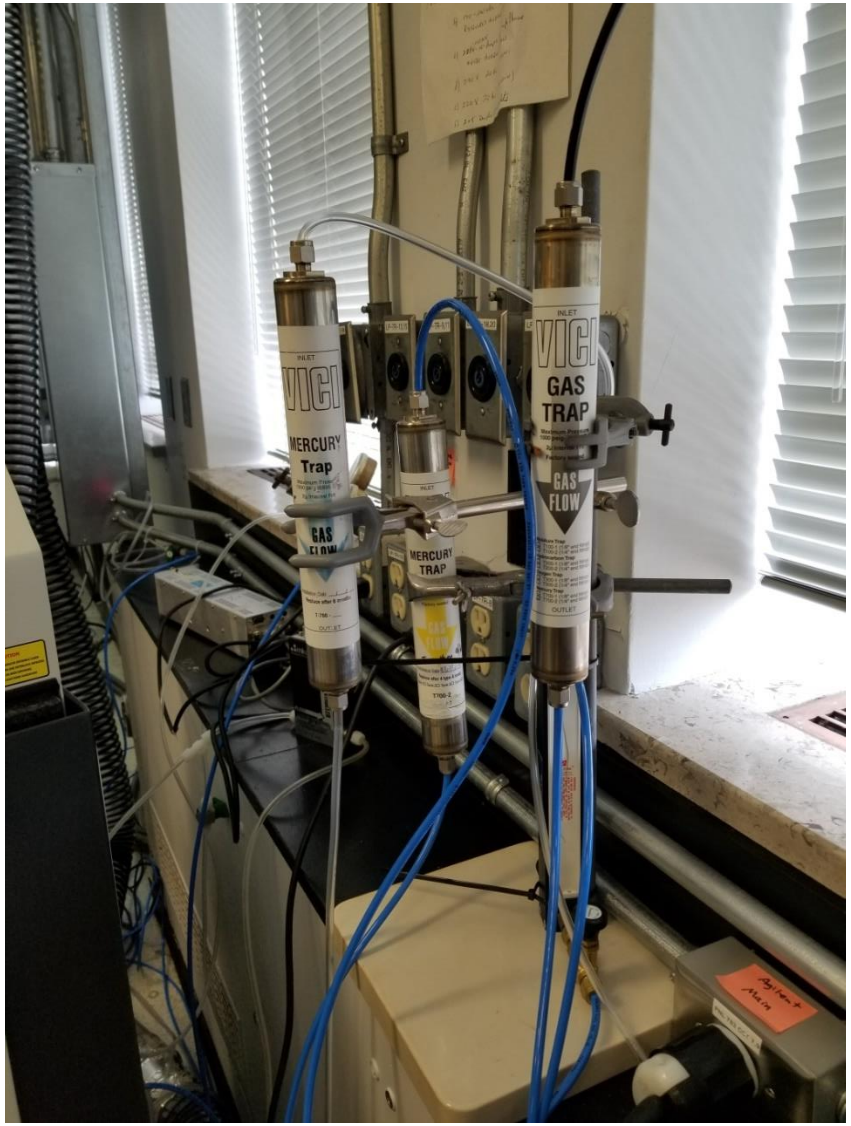
- Tendency for higher counts correlate with holes & mounts
- no differences between
  - empty holes
  - holes filled with mounts


68000
64000
60000
56000
52000
48000
44000
40000
56_cps


3600
3200
2800
2400
2000
1600
1200
800
400
202_cps

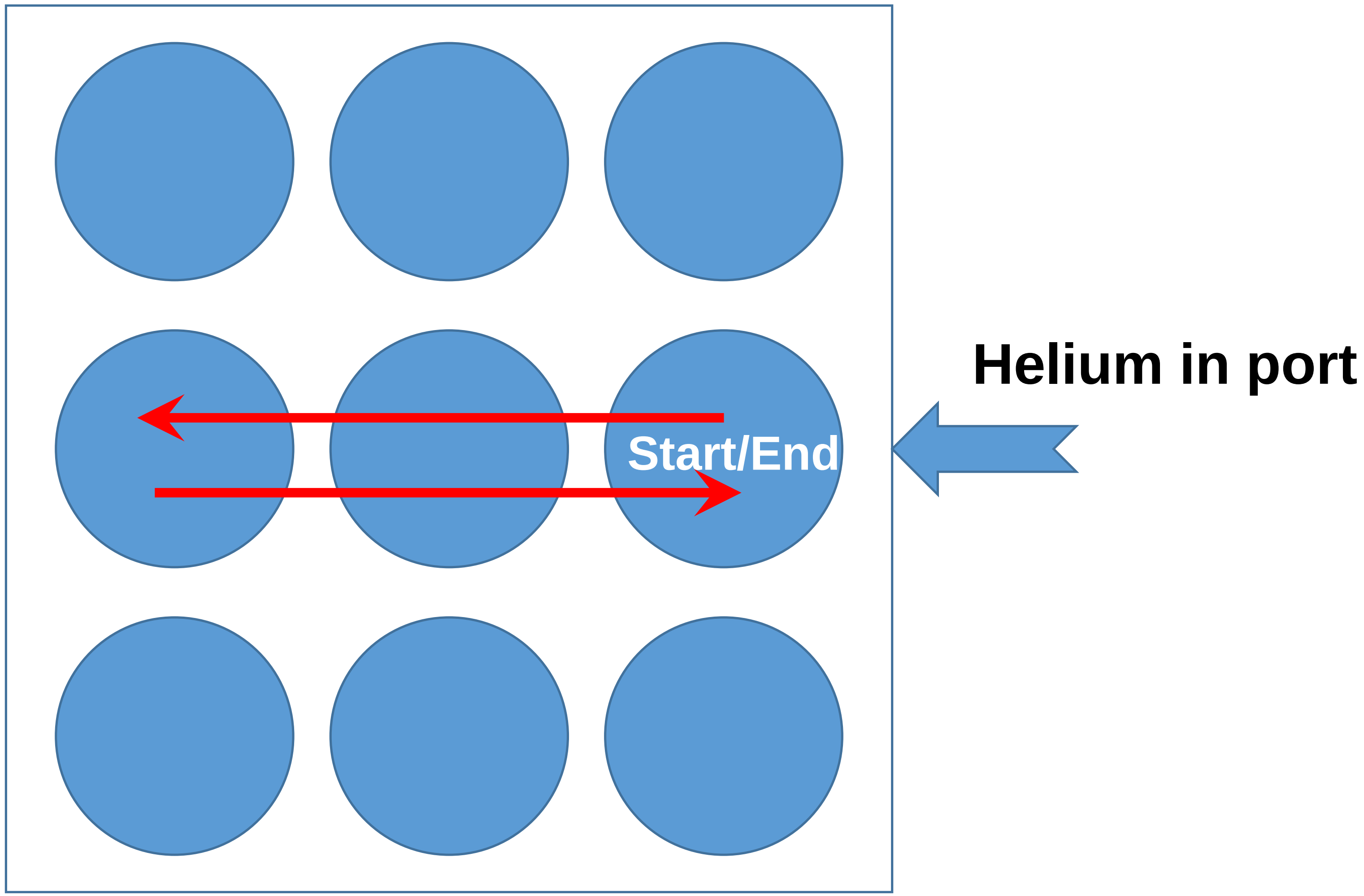
Vici Hg traps

- Flow rate up to 25 lpm allows all ICP-MS gases to be filtered
- Filtering He also reduces Hg background
- Hg backgrounds (^{201}Hg) as low as 36 cps have been attained, allowing meaningful implementation of ^{204}Pb correction

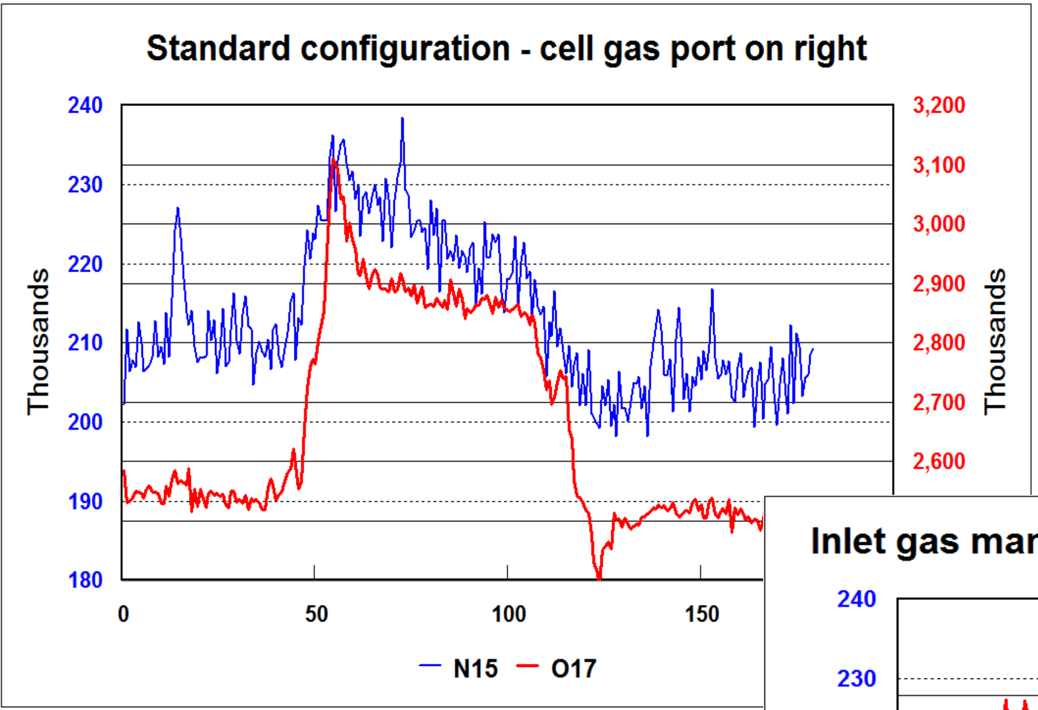


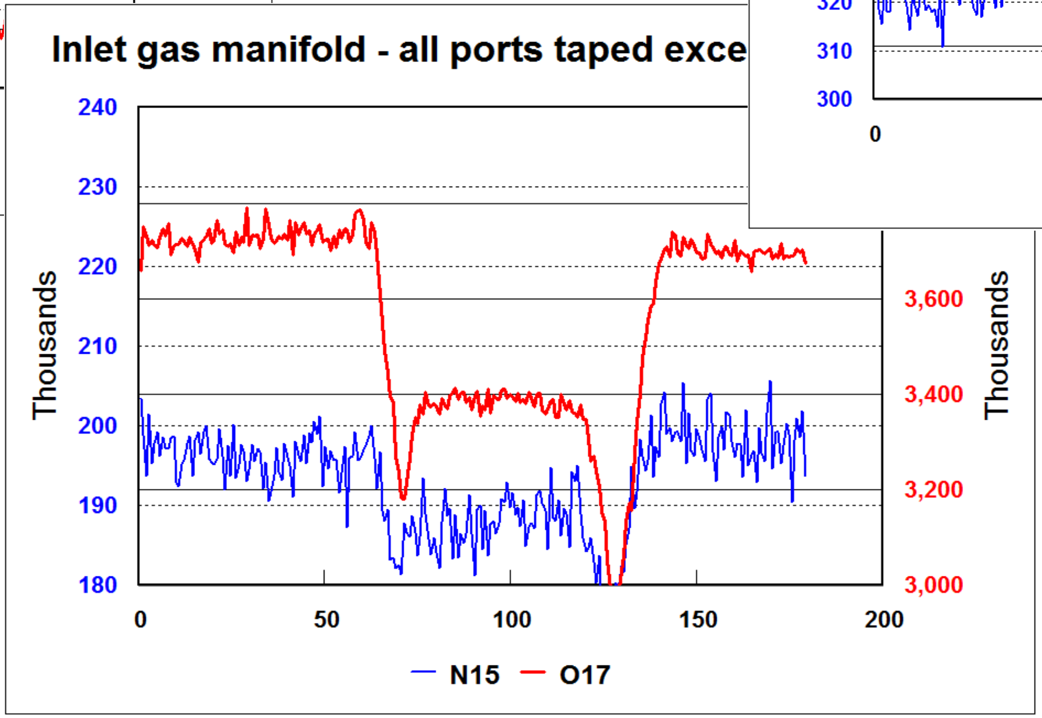
Solution
In-cell gas manifold

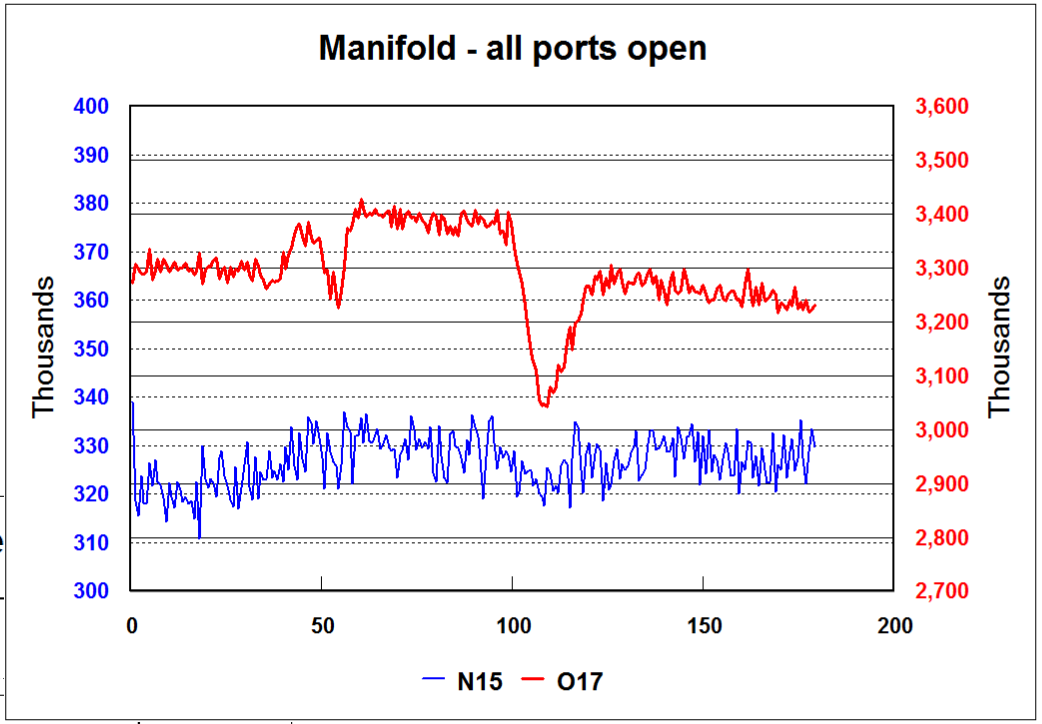
Stage movement sequence



In-cell gas manifold







Take home messages

- Immense care must be taken to ensure that operating conditions, especially laser focus, are identical for sample and standard
- Rigorous degassing of sample mounts and flushing of the sample cell are required to minimise cell contaminant gas related biases
- A cell gas distribution manifold greatly reduces contaminant gas variability within the cell.
- Mounting of samples and standards in the same mount is one way to minimise differences in both laser focus and spatial variations in contaminant gas concentrations, especially H_2O in the sample cell.