ETH zürich

U/Pb dating of CA-treated zircons obtained by LA-ICP-MS and ID-TIMS

von Quadt[1], and I. Peytcheva[1,2]

1: Department of Earth Sciences, Institute of Geochemistry and Petrology, ETH Zurich, Switzerland

2: Bulgarian Academy of Science, Geological Institute, Sofia, Bulgaria

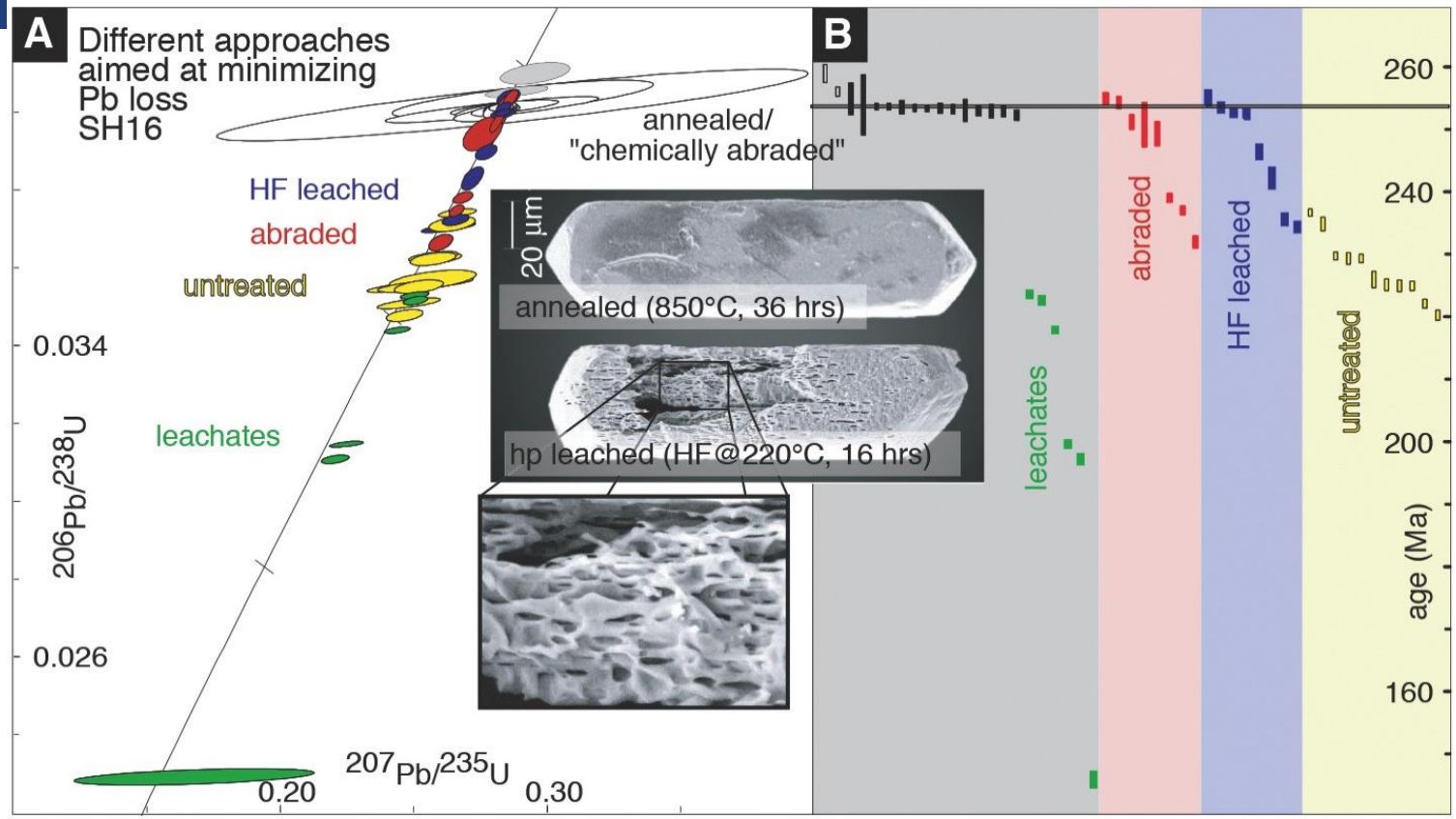
- Short introduction to the CA technique
- TIMS – results of CA and non-CA measurements
- Laser parameter at ETH Zurich
- Ablation behaviour of CA and non-CA treated zircon standards
- LA-ICP-MS – results of CA and non-CA treated geological samples (0 – 600 Ma)
- Conclusion

Outline

- Annealing at 850 ºC, 48 h
- Leaching with conc. HF, 2 - 12 h, 180 ºC
- Rinse with IR-H_2O, several times
- Leaching/washing with 6N HCL, hot plate, 80 ºC, 24 h
- Rinse with IR-H_2O, several times

- Total elimination of discordance by Pb loss
- Removing zircon domains with “lead loss” component
- J. Mattinson, 2005, Chemical Geology, 220, 47 - 66

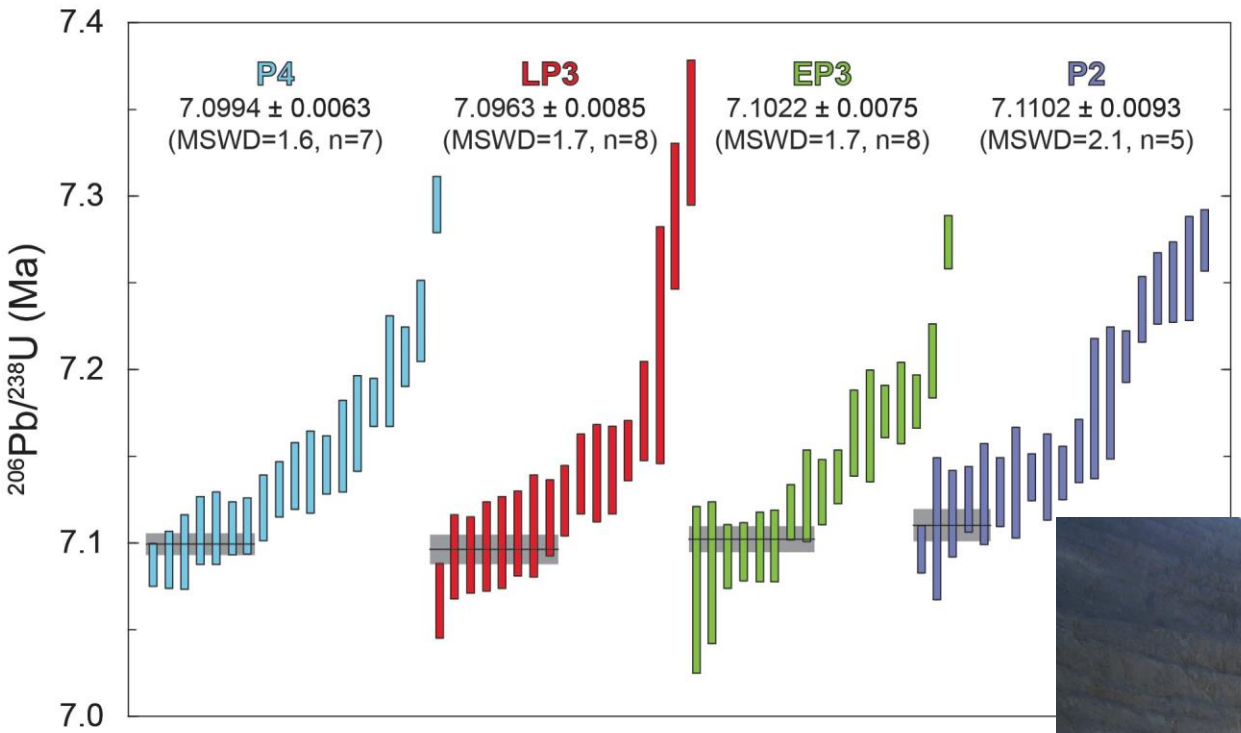
CA - technique



Concordia diagram (A) and ranked ages (B) of zircon analyses from sample SH16(18) obtained from different approaches aimed at minimizing the effects of Pb loss. SEM image of a zircon shows the effects of chemical abrasion following annealing (uncertainties are given at the 95% confidence level).

Mundil, R. et al. (2004). Science 305, 1760.

CA-technique: CA-ID-TIMS example



Zircon single grain analysis

CA-treated zircons

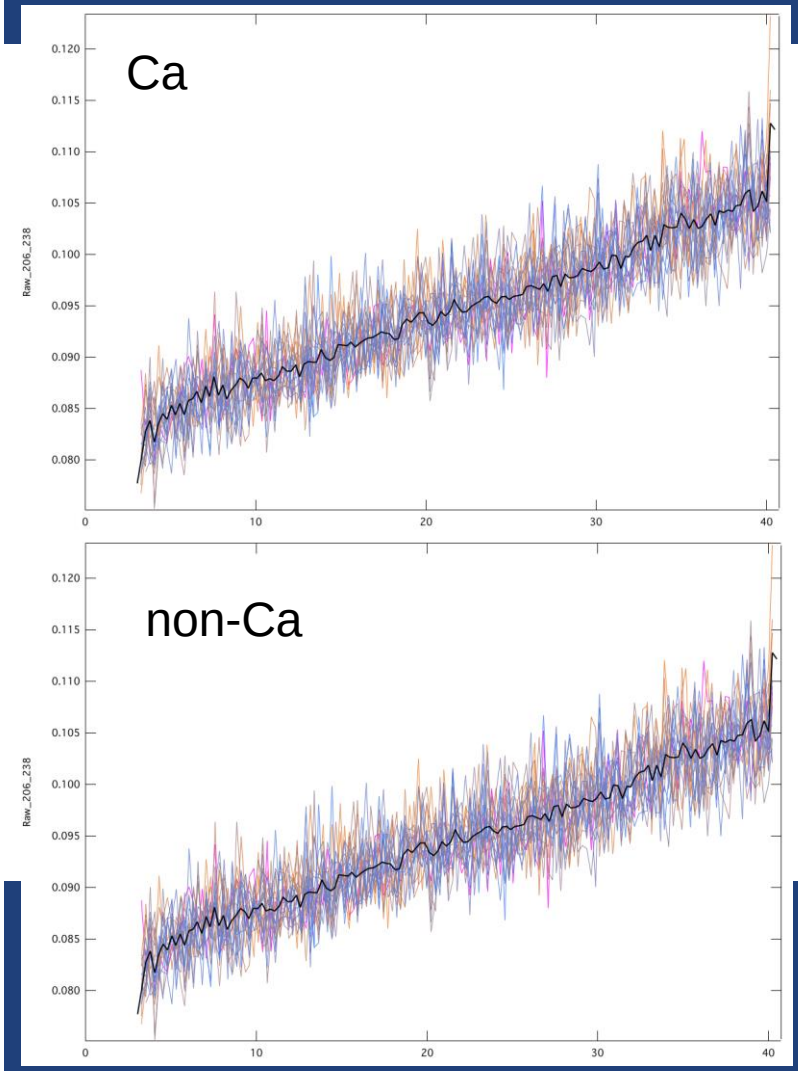
Result:
- 5-8 grains overlapping
- time of intrusion
- All intrusion are co-genetic within 10’000 years

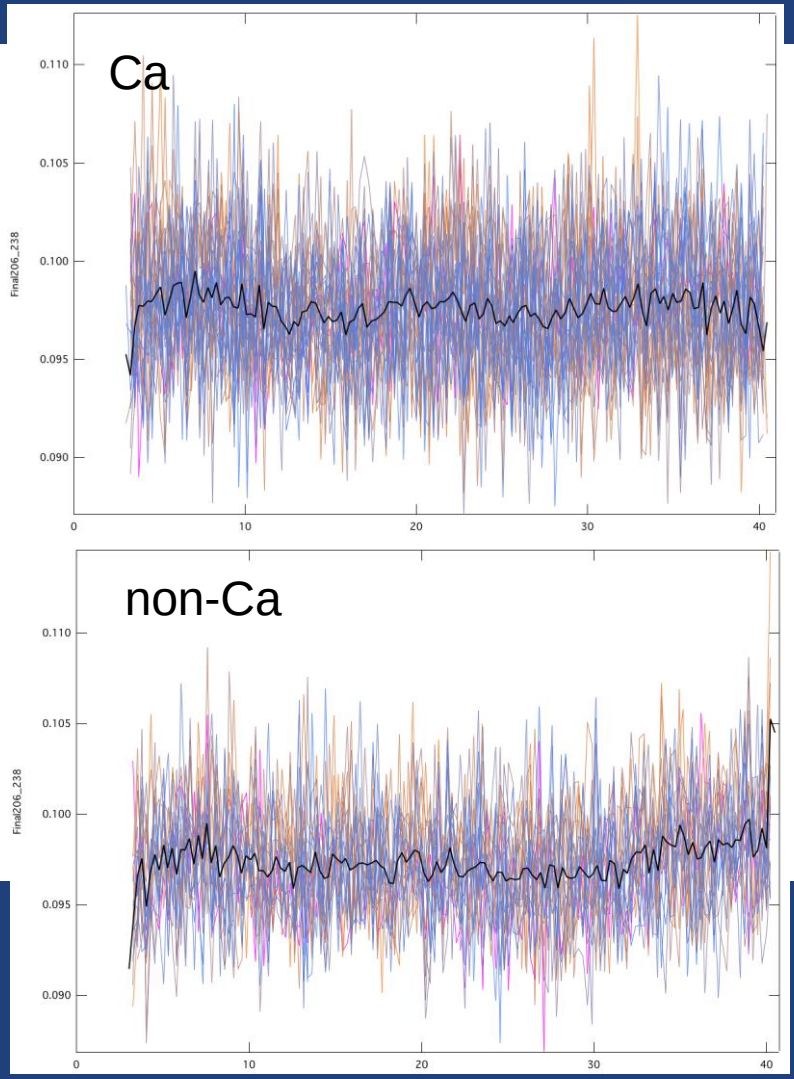
Alumbrera (Argentina) – individual intrusion

Cu-(Au) porphyry, see Y. Burret, Friday 21st August, Session 12e, South Hall 2, 10.30 :

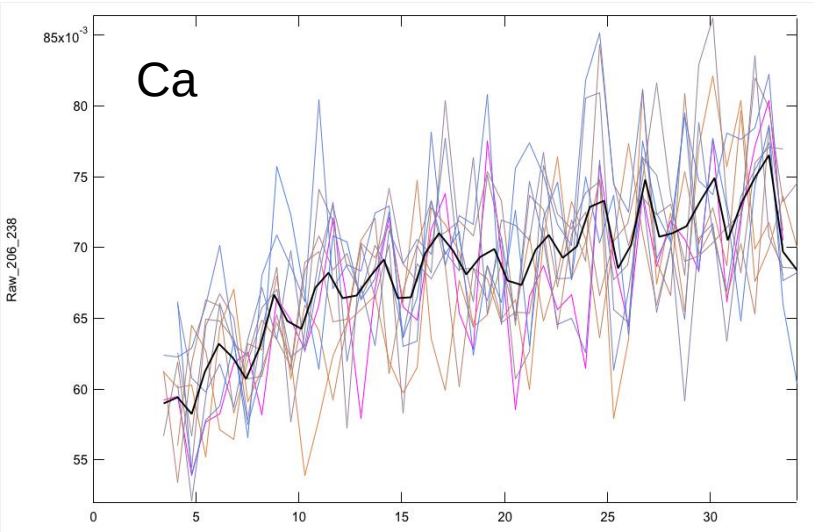
Laser ablation system	
Make, Model & type	Resonetics Resolution 155
Ablation cell & volume	Laurin Technics 155, constant geometry, aerosol dispersion volume < 1 cm^3
Fluence ($J.cm^{-2}$)	~ 2.0 $J.cm^{-2}$
Repetition rate (Hz)	4 Hz
Spot size (um)	30 um
Sampling mode / pattern	Single hole drilling, 5 cleaning pulses
Carrier gas	100% He, Ar make-up gas combined inside ablation cell funnel.
He Cell carrier gas flow (l/min)	0.7l/min
ICP-MS Instrument	
Make, Model & type	Thermo Element XR SF-ICP-MS
Sample introduction	Ablation aerosol only, squid aerosol homogenization device
Make-up gas flow (l/min)	0.95l/min Ar
Detection system	Single detector triple mode SEM, analog, Faraday
Masses measured	202, 204, 206, 207, 208, 232, 235, 238
Integration time per peak (ms)	12 ms (masses 202, 204), 20 ms (masses 208, 232, 235, 238), 40 ms (masses 206, 207)

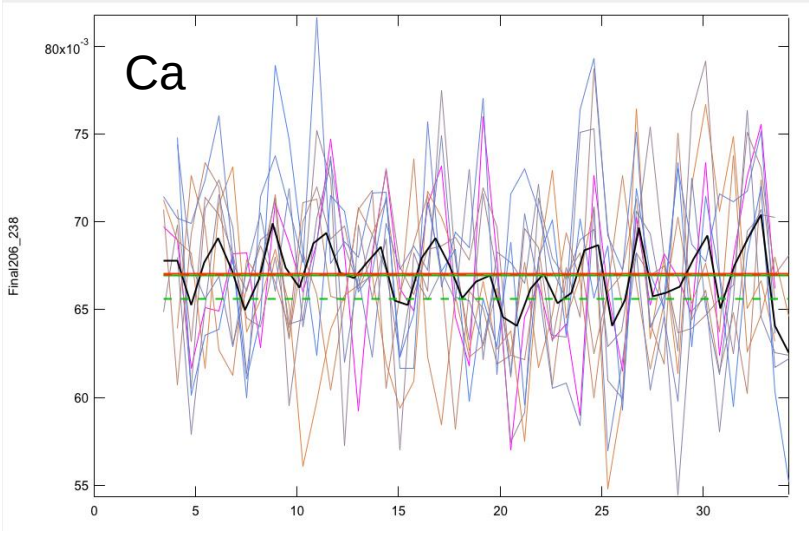
Equipment at ETH Zurich

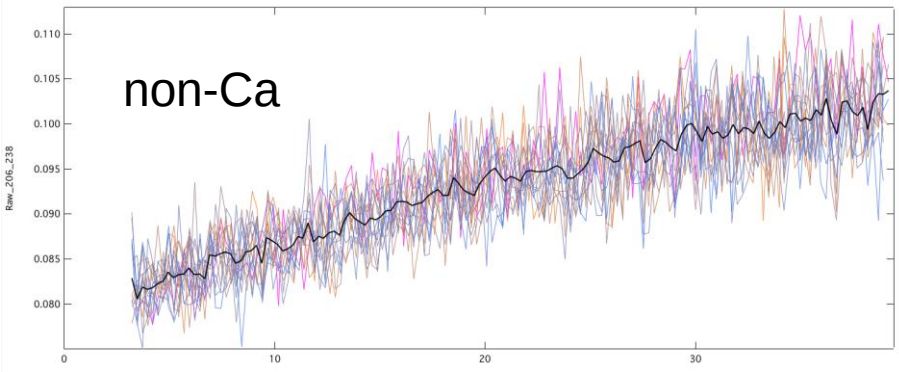


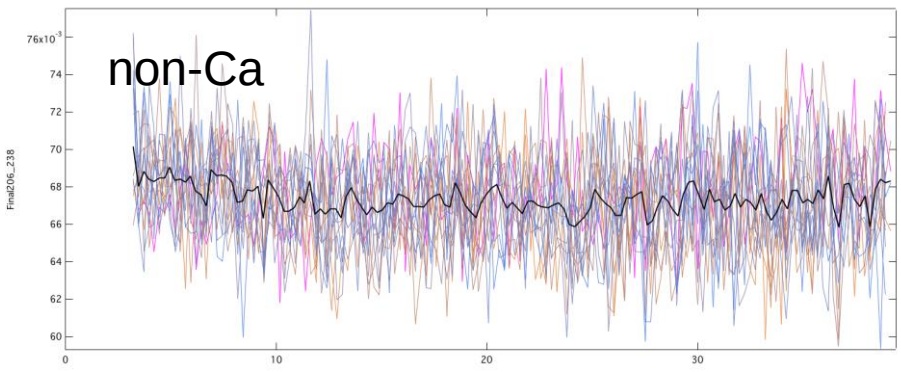


GJ1 ablation behaviour

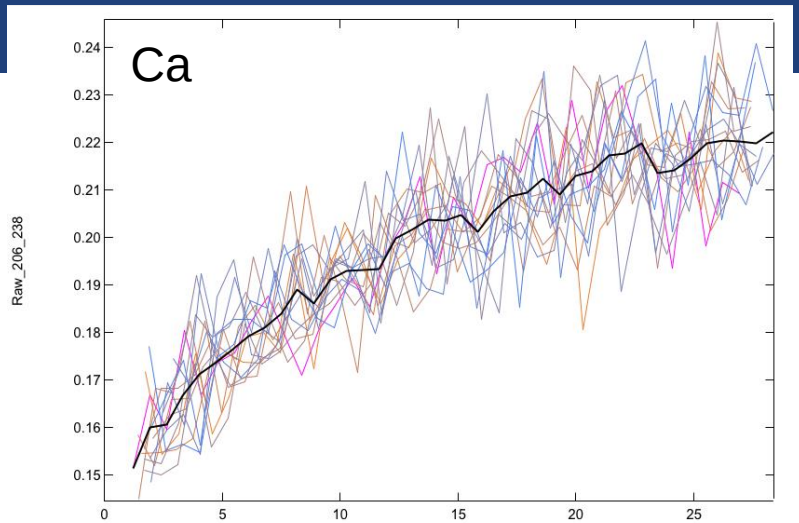


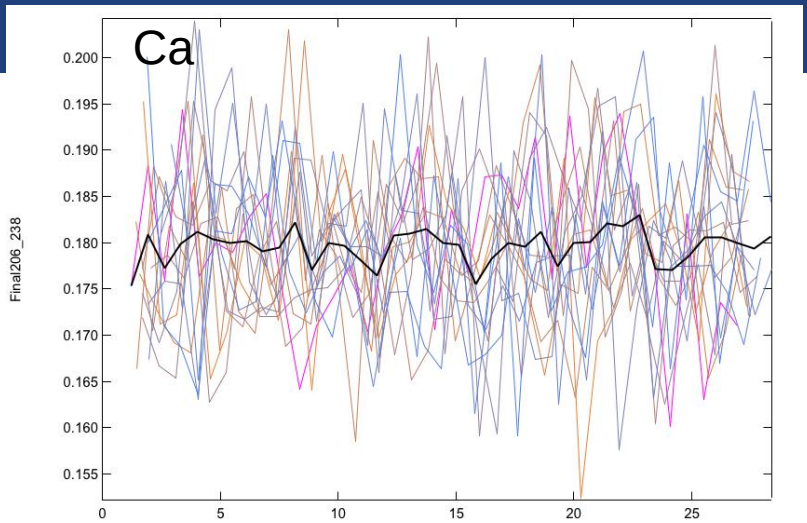


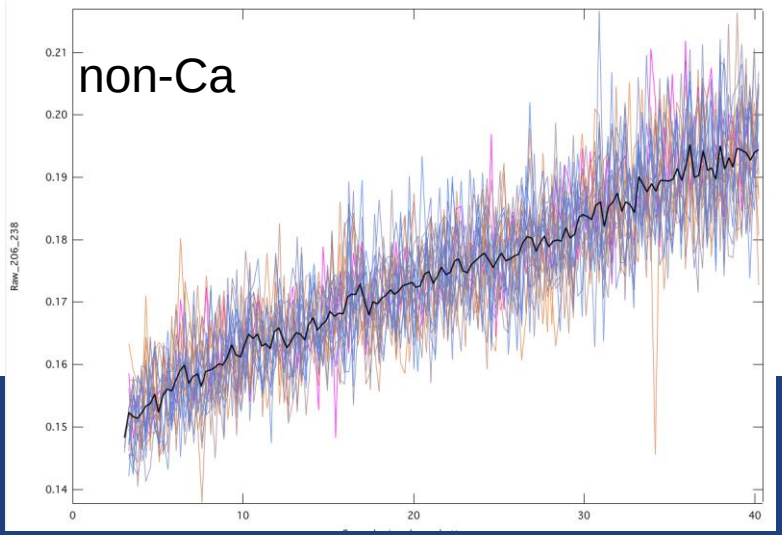


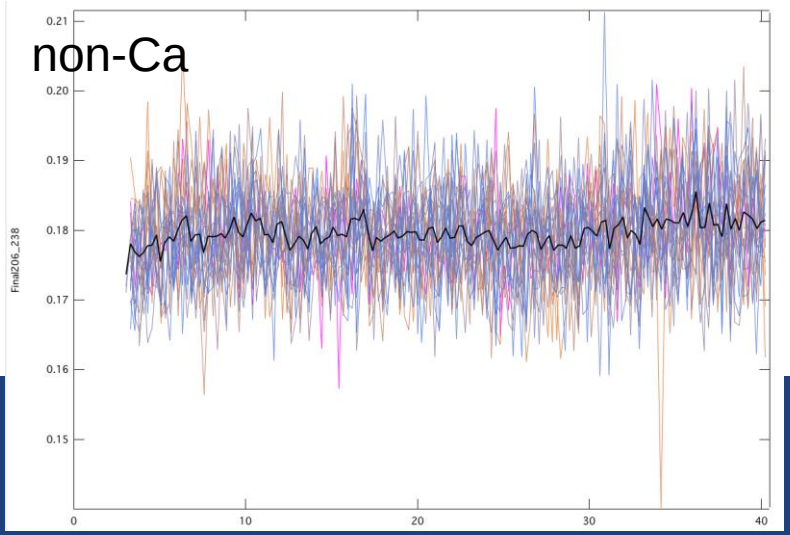


Temora zircon

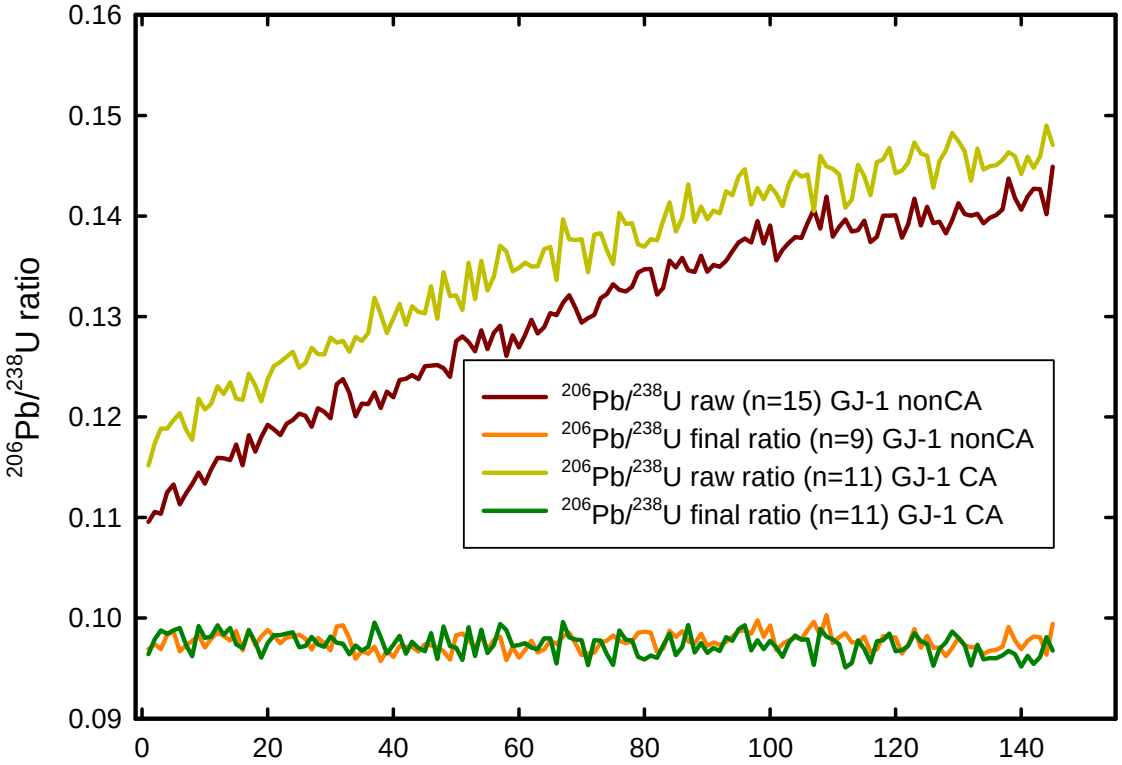






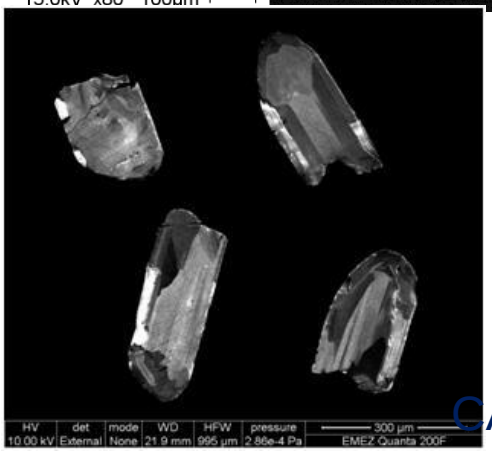


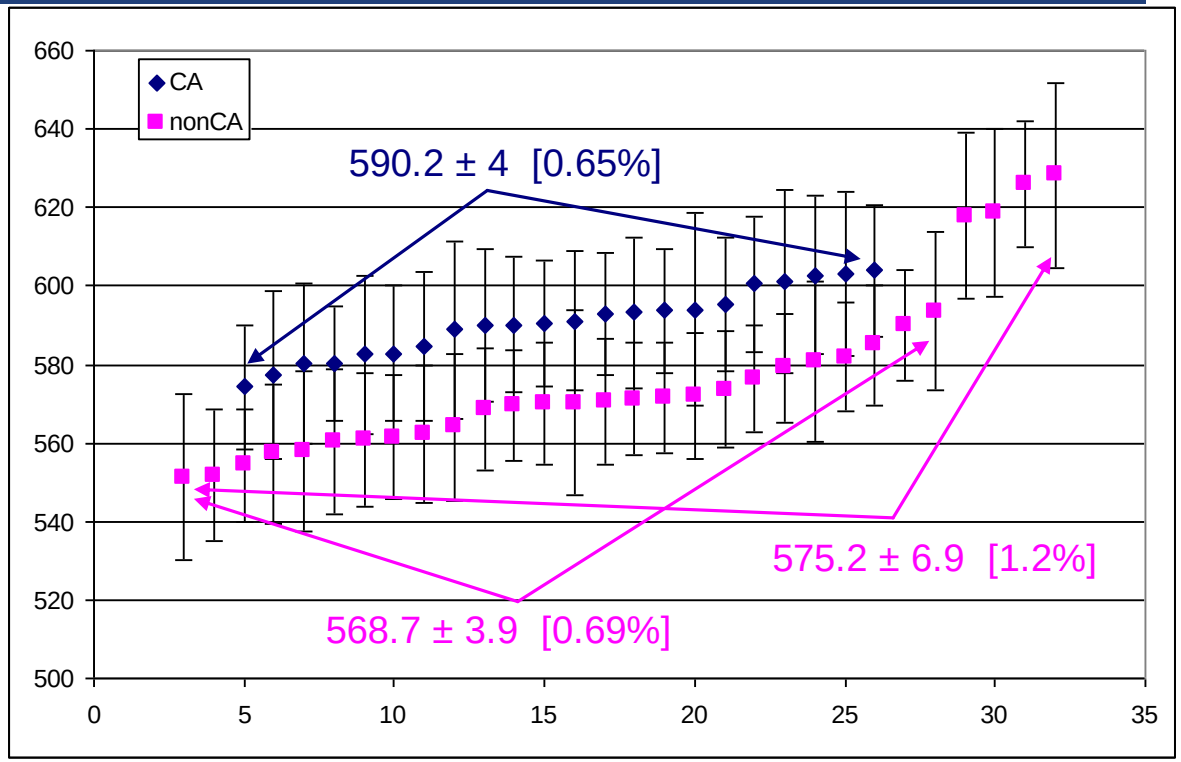
91500 zircon



Comparison CA- and non-CA treated GJ-1 zircon

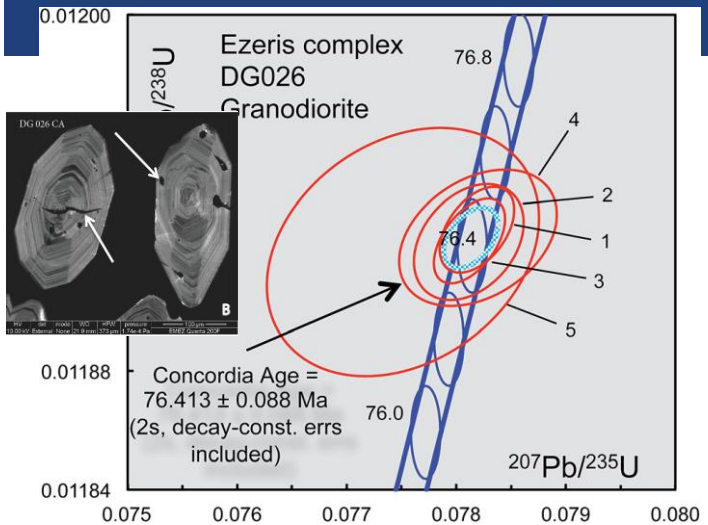
Similar ablation behaviour of CA- and non CA treated GJ-1 zircon standard

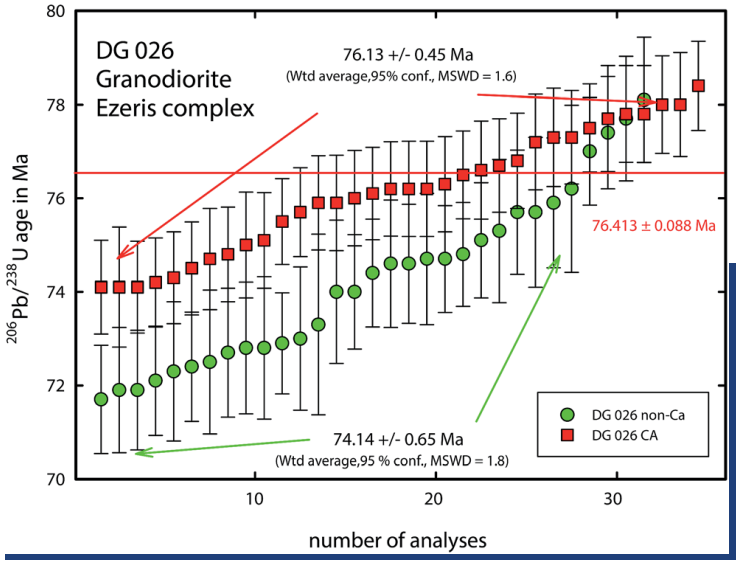




Non-CA treated zircons: individual $^{206}Pb/^{238}U$ ages between 551±20 Ma and 628±23 Ma with average age 566±4 Ma.
CA-treated zircons: Concordia age of 590±4 Ma, whereas the individual zircons are older than 570 Ma ($^{206}Pb/^{238}U$ age from 574±16 Ma to 604±16 Ma)

Metadiorite Struma Unit (Western Bulgaria); U 40 and 370 ppm





Sample DG026 represents a granodiorite from the Romanian part of the >1600 km long Cretaceous magmatic belt in Eastern Europe

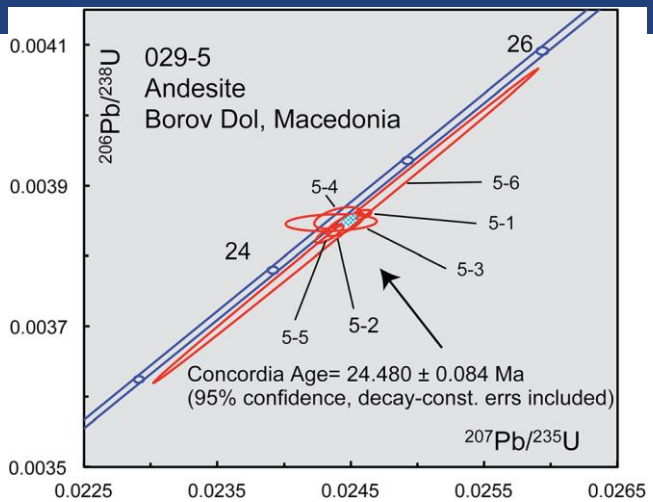
Uranium concentrations vary between 498 ppm and 682 ppm

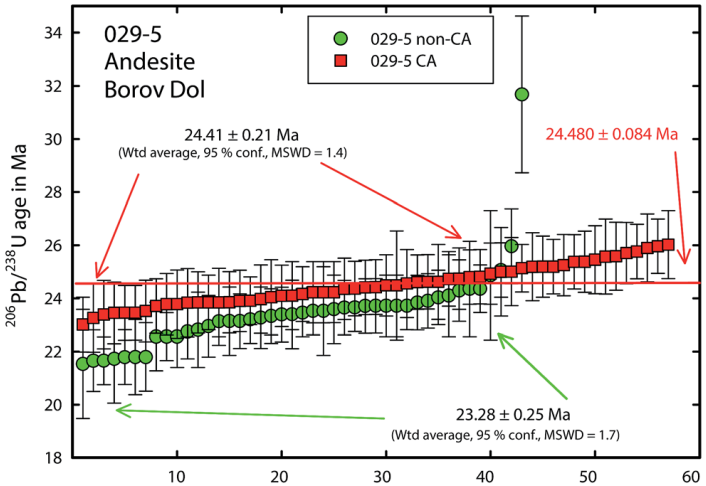
CA-ID-TIMS yields a concordia age of 76.413± 0.088 Ma.

Difference in $^{206}Pb/^{238}U$ ages acquired from non-CA and CA treated zircons that are 74.14±0.65 Ma and 76.13±0.45 Ma (95% conf.), respectively .

Scatter of the CA treated zircons is smaller.

Mesozoic magmatic zircons





Andesite of the Cu-Au porphyry deposit at Buchim, (Macedonia).

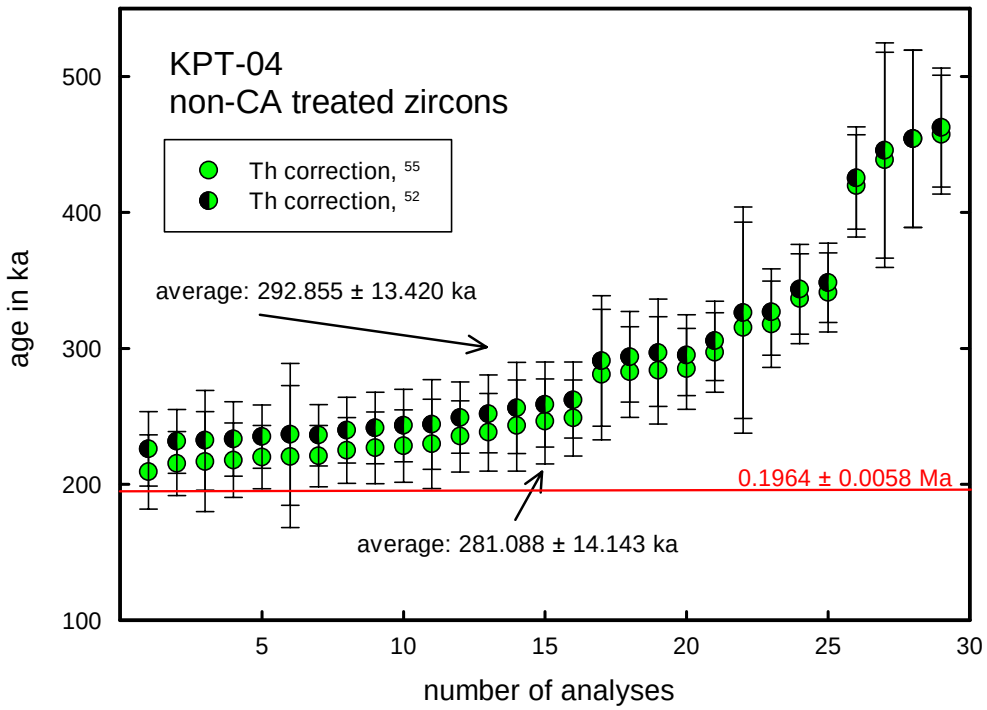
Zircons: high uranium between 834 ppm and 2298 ppm

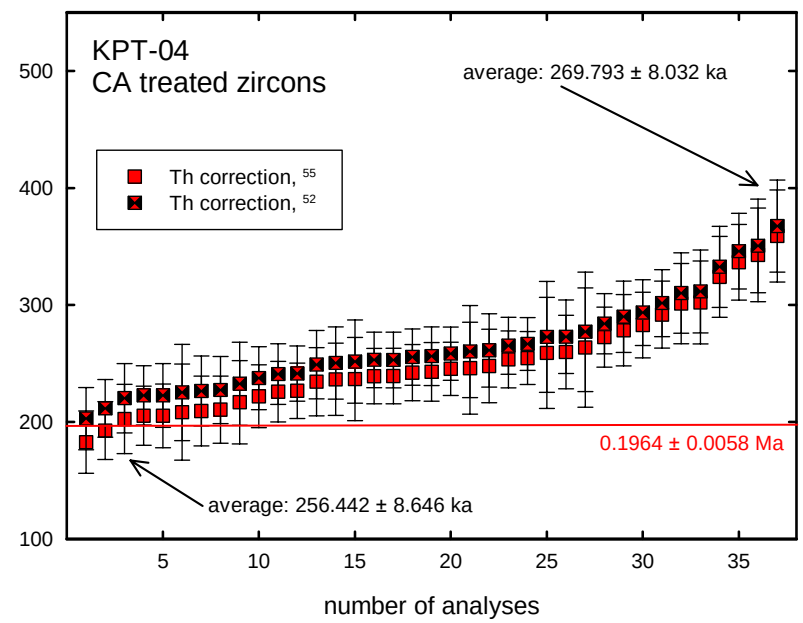
CA-ID-TIMS age is 24.480±0.048 Ma.

The obtained LA-ICP-MS $^{206}Pb/^{238}U$ average age of the CA-treated zircons is 24.41±0.21 Ma and they overlap perfectly with the ID-TIMS data, whereas the non-CA-treated zircons yield an age of 23.50±0.25 Ma.

An important observation is that CA treatment appears to reduce age scatter. Scatter of the $^{206}Pb/^{238}U$ ages of 0.29 Ma for CA-treated zircons is lower, compared to a greater scatter (0.73 Ma) for non-CA zircons.

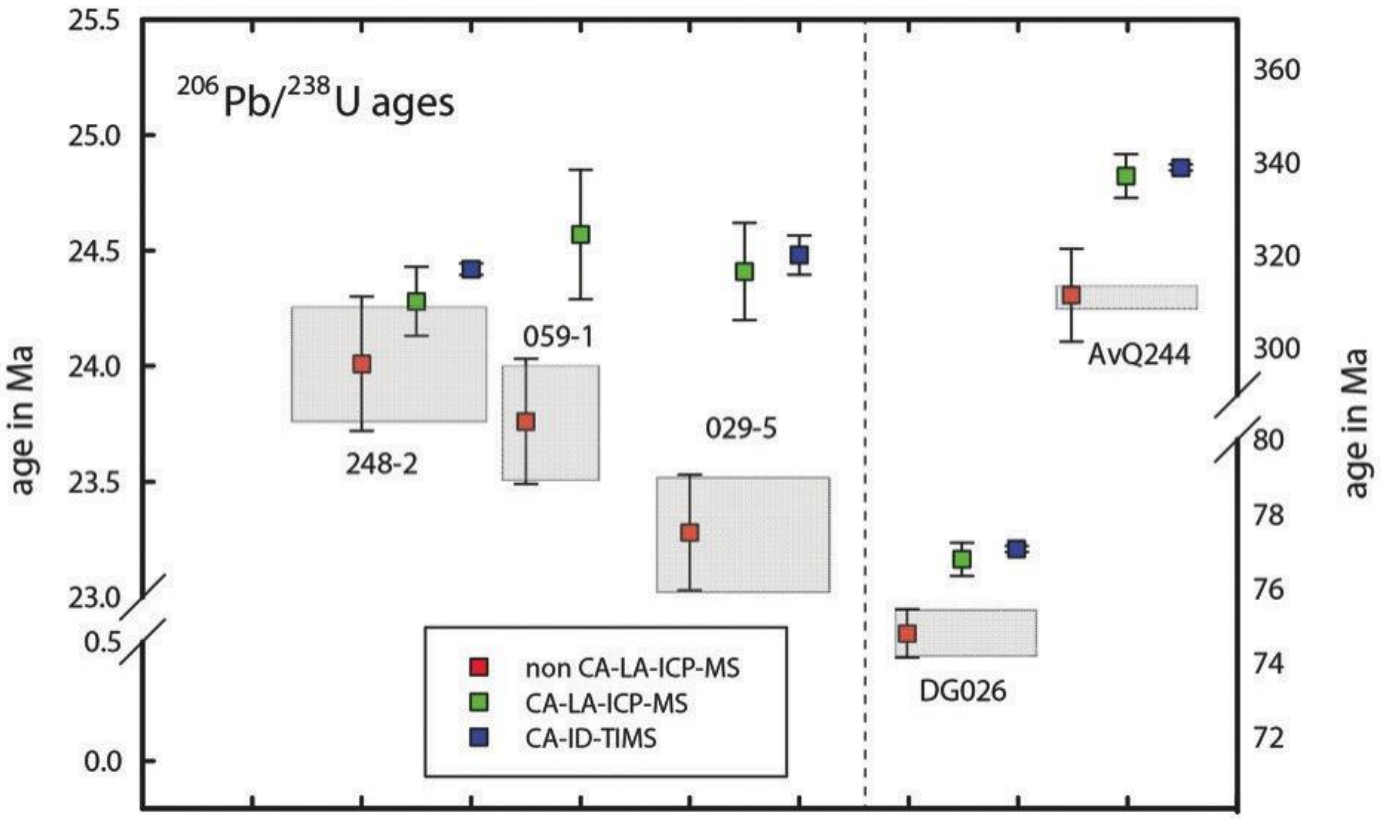
Cenozoic magmatic zircons





Kos island, Greece

Quaternary sample (Rhyolite)



Summary non-CA, CA-LA-ICP-MS and CA-ID-TIMS ages,

grew box represents the uncertainty of LA-ICP-MS measurements (Koslar et al., 2013)

Von Quadt et al. (2014), JAAS, doi: 10.1039/c4ja00102h

- The CA procedure employed on zircon grains leads to a U/Pb age precision of 0.1 – 0.2 % (CA-ID-TIMS) and to < 1.5 % (CA-LA-ICP-MS).
- $^{206}Pb/^{238}U$ dates obtained by CA-ID-TIMS and CA-LA-ICP-MS overlap within the analytical uncertainty.
- LA-ICP-MS ages for zircon grains, which have been treated by chemical abrasion (CA), show less scatter of the U/Pb data compared to the non-CA treated zircon set.
- The CA technique efficiently eliminates discordance caused by Pb loss or crystal damage caused by the alpha dose; reduction of the data scatter, the relative error uncertainties up to 50%.
- The differences of the $^{206}Pb/^{238}U$ weighted mean ages obtained from CA- and non-CA treated zircon crystals are in a range up to 4 - 8%.

Summary and outlook

CL zircon images after Chemical Annealing

Annealing and leaching – AvQ 244 Granite (300 Ma), DG 026 Granodiorite (80 Ma)

March 2014, Dept. E.Sci, ETH Zurich					Ages							
Identifier	ICPMS Type	quantity	Uppm[1]	Th/U	207Pb/206Pb	2s abs	206Pb/238U	2s abs	207Pb/235U	2s abs	208Pb/232Th	2s abs
non-CA[2]												
GJ-1	Elan	n = 64	386	0.0286	614	19.9	600.2	2.3	603.7	4.2	603.2	13.4
Plesovice	Elan	n = 22	721	0.0566	402	61.2	343.4	2.8	351.9	9.3	381.0	30.3
non-CA[2]												
GJ-1	Element-XR	n = 36	318	0.0214	609	2.8	600.7	0.7	602.3	0.5	600.3	5.6
Plesovice	Element-XR	n = 9	595	0.1003	339	5.6	335.1	0.6	335.4	0.7	334.5	4.3
Temora 2	Element-XR	n = 13	152	0.4748	414	8.0	419.1	1.2	418.8	0.8	417.1	6.8
91500	Element-XR	n = 18	76	0.5572	1068	5.1	1066.3	2.3	1066.3	2.6	1060.3	7.0
CA[3]												
GJ-1	Element-XR	n = 30	326	0.0363	607	3.7	599.6	1.3	601	1.4	603.6	7.2
Temora 2	Element-XR	n = 10	176	0.4509	419	12.5	417.2	1.6	418.6	2.9	412.3	6.5
non CA[2]												
Temora 2[4]	Element-XR	n = 24	89	0.45	405.5	7.4	419.1	1.6	417.4	2.1	415.8	4.6

[1] concentration uncertainty c.20%
[2] data not treated by chemical annealing, primary zircon standard GJ-1 non-CA
[3] data are treated by chemical annealing, primary zircon standard GJ-1, CA
[4] non CA Temora is referenced to a CA GJ-1

Selected results of CA and non-CA treated zircon standard measurements