RADIOCARBON DATING OF MORTAR: CASE STUDY OF THE AQUEDUCT IN SKOPJE

Andreja Sironić*, Damir Borković*, Jadranka Barešić*, Ines Krajcar Bronić*, Alexander Cherkinsky**, Ljiljana Kitanovska***

MET ARH

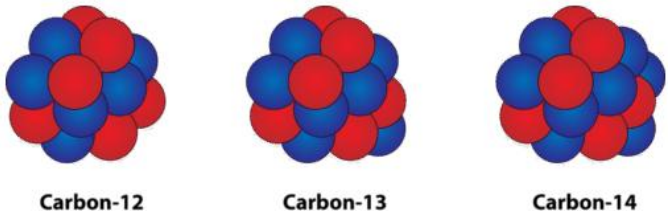
31.11.-1.12.2017.
Zagreb, Croatia

*Laboratory for Low Level Radioactivities, Ruđer Bošković Institute, Zagreb, Croatia
**Center for Applied Isotope Studies, The University of Georgia, Athens, Georgia, USA
***National Institution Conservation Centre, Skopje, Macedonia

Outline

- INTRO
  - Carbon isotopes
  - The problem of dating mortar and different philosophies attached
  - The Aqueduct in Skopje
- Experiment: CRYOSONIC separation + INCLUSION
- Results
- Discussion and conclusions

Carbon isotopes – in short

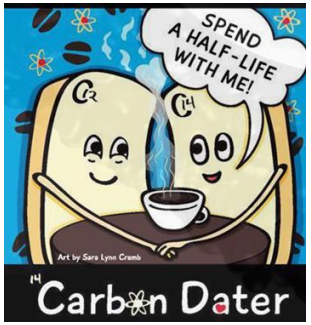


^{13}C

- 1.1%
- stable
- Depends on type of material and reactions during its formation
- Delta value ($\delta^{13}C$)– relative to PDB (permill)

^{14}C (Radiocarbon)

- 10^{-10} %
- Radioactive ($t_{1/2}$ 5730 years)
- Formed in stratophere, a part of atmospheric CO_2 and biosphere
- a^{14}C (pMC)



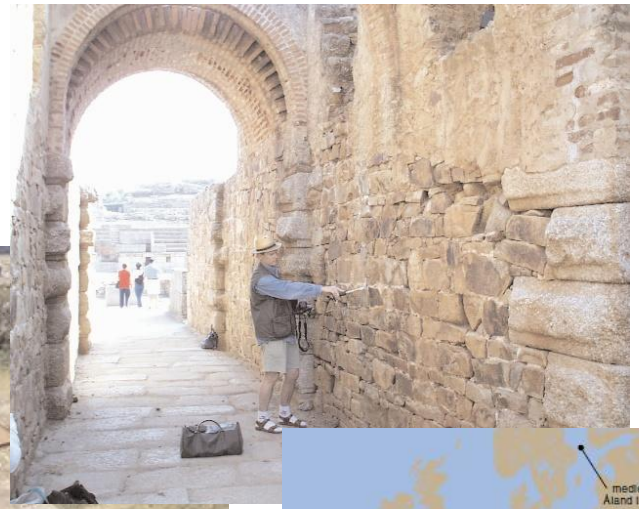
How is the sample prepared for analysis at LNA

1. From carbonates - producing CO_2 in reaction with acid (HCl, H_3PO_4)

   From organics – oxidation with CuO to CO_2
2. A portion of CO_2 is saved for $\delta^{13}C$ (mass spectrometry, IRMS)
3. A portion of CO_2 is turned to graphite (C) and pressed into aluminum target for $a^{14}C$ (accelerator mass spectrometry, AMS)

Dating of mortar by the radiocarbon

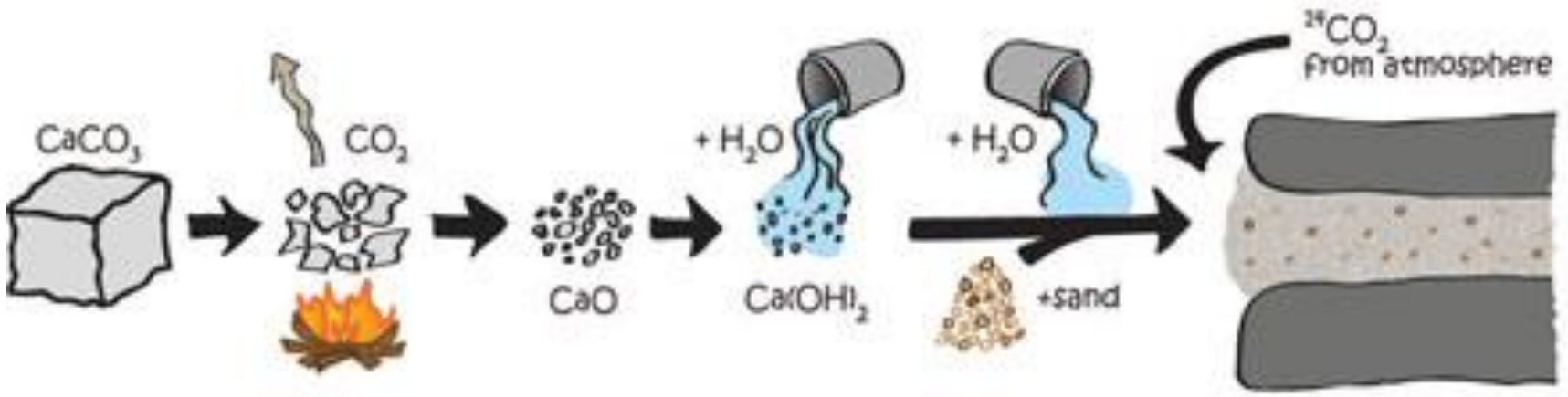
- The mortar dating as old as the Radiocarbon method



- "It works!... Unless it doesn't…"

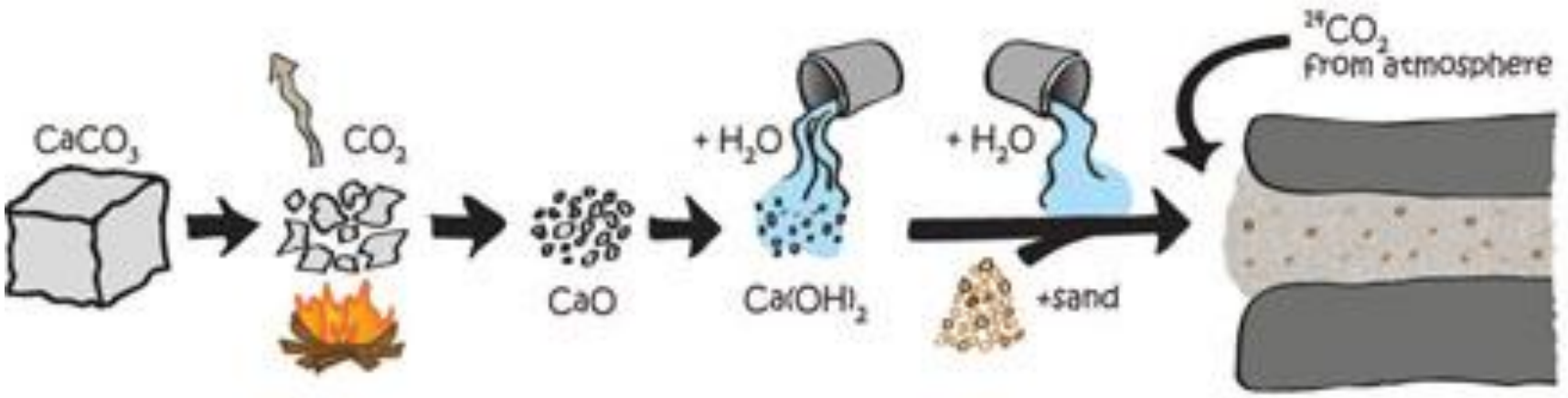
The problem of dating mortar and different philosophies attached

- The principle of mortar dating



The problem of dating mortar and different philosophies attached

- The principle of mortar dating



$Ca(OH)_2 + C^*O_2(g, atm) \rightarrow CaC^*O_3 + H_2O$

The problems of dating mortar

The problems:

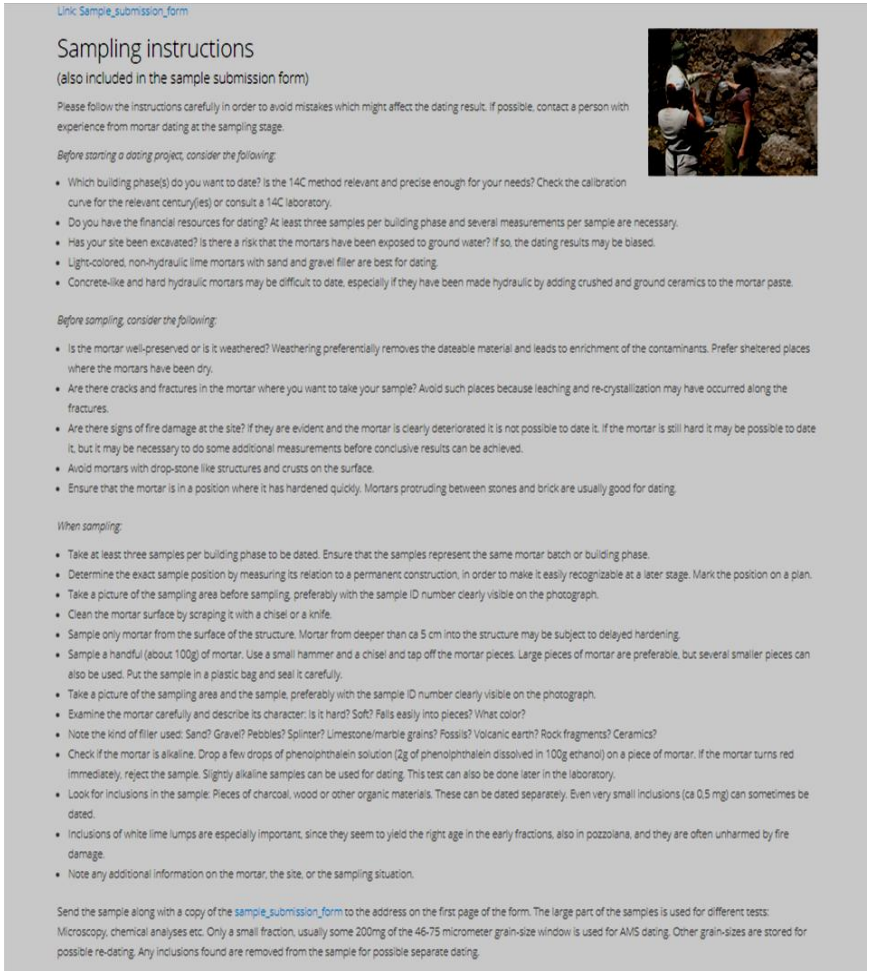
- Unreacted old carbonate – „dead carbon" contamination
- Elements - uptake of carbon in the form of dissolved inorganic carbonates – cracks
- Burning of building – yields new carbonate
- No deeper than 5 cm – delayed hardening
- If too alkaline – still uptakes CO_2 from the air

http://www.mortardating.com/method

When dating mortar it is far better to…

- Date organic residues
- But if you really want to: Inclusions of white lumps - the most reliable… but…

Or follow the instructions…



Link Sample_submission_form

Sampling instructions

(also included in the sample submission form)

Please follow the instructions carefully in order to avoid mistakes which might affect the dating result. If possible, contact a person with experience from mortar dating at the sampling stage.

Before starting a dating project, consider the following:

- Which building phase(s) do you want to date? Is the 14C method relevant and precise enough for your needs? Check the calibration curve for the relevant century(ies) or consult a 14C laboratory.
- Do you have the financial resources for dating? At least three samples per building phase and several measurements per sample are necessary.
- Has your site been excavated? Is there a risk that the mortars have been exposed to ground water? If so, the dating results may be biased.
- Light-colored, non-hydraulic lime mortars with sand and gravel filler are best for dating.
- Concrete-like and hard hydraulic mortars may be difficult to date, especially if they have been made hydraulic by adding crushed and ground ceramics to the mortar paste.

Before sampling, consider the following:

- Is the mortar well-preserved or is it weathered? Weathering preferentially removes the dateable material and leads to enrichment of the contaminants. Prefer sheltered places where the mortars have been dry.
- Are there cracks and fractures in the mortar where you want to take your sample? Avoid such places because leaching and re-crystallization may have occurred along the fractures.
- Are there signs of fire damage at the site? If they are evident and the mortar is clearly deteriorated it is not possible to date it. If the mortar is still hard it may be possible to date it, but it may be necessary to do some additional measurements before conclusive results can be achieved.
- Avoid mortars with drop-stone like structures and crusts on the surface.
- Ensure that the mortar is in a position where it has hardened quickly. Mortars protruding between stones and brick are usually good for dating.

When sampling:

- Take at least three samples per building phase to be dated. Ensure that the samples represent the same mortar batch or building phase.
- Determine the exact sample position by measuring its relation to a permanent construction, in order to make it easily recognizable at a later stage. Mark the position on a plan.
- Take a picture of the sampling area before sampling, preferably with the sample ID number clearly visible on the photograph.
- Clean the mortar surface by scraping it with a chisel or a knife.
- Sample only mortar from the surface of the structure. Mortar from deeper than ca 5 cm into the structure may be subject to delayed hardening.
- Sample a handful (about 100g) of mortar. Use a small hammer and a chisel and tap off the mortar pieces. Large pieces of mortar are preferable, but several smaller pieces can also be used. Put the sample in a plastic bag and seal it carefully.
- Take a picture of the sampling area and the sample, preferably with the sample ID number clearly visible on the photograph.
- Examine the mortar carefully and describe its character: Is it hard? Soft? Falls easily into pieces? What color?
- Note the kind of filler used: Sand? Gravel? Pebbles? Splinter? Limestone/marble grains? Fossils? Volcanic earth? Rock fragments? Ceramics?
- Check if the mortar is alkaline. Drop a few drops of phenolphthalein solution (2g of phenolphthalein dissolved in 100g ethanol) on a piece of mortar. If the mortar turns red immediately, reject the sample. Slightly alkaline samples can be used for dating. This test can also be done later in the laboratory.
- Look for inclusions in the sample: Pieces of charcoal, wood or other organic materials. These can be dated separately. Even very small inclusions (ca 0,5 mg) can sometimes be dated.
- Inclusions of white lime lumps are especially important, since they seem to yield the right age in the early fractions, also in pozzolana, and they are often unharmed by fire damage.
- Note any additional information on the mortar, the site, or the sampling situation.

Send the sample along with a copy of the sample_submission_form to the address on the first page of the form. The large part of the samples is used for different tests: Microscopy, chemical analyses etc. Only a small fraction, usually some 200mg of the 46-75 micrometer grain-size window is used for AMS dating. Other grain-sizes are stored for possible re-dating. Any inclusions found are removed from the sample for possible separate dating.

http://www.mortardating.com/method

How to differ the old and the „new" calcium carbonate

- **Limestone/dolomite (old, no ^{14}C)**

harder, white, transparent, slow reaction with acid

- **Ca-carbonate formed during carbonation of slaked lime (new, ^{14}C for dating)**

soft, white, powdery, quickly reacts with acid

Philosophies…

- Selecting successive CO_2 gas fractions (the first fraction –for dating; „The Aarhus" method[1])
- Breaking of mortar and selecting fractions according to size and ability to disperse in water (the smallest particles with highest specific surface – carbon for dating; „The Italian" method[2])

[1] Ringbom et al, Radiocarbon (2014) 619

[2] Marzaioli et al, Nucl. Instr. Meth. Phys B (2013) 246

The Aqueduct in Skopje

The project for conservation and restoration of the Aqueduct

(microscopic investigation, XRD, XRF, mineralogy, density, porosity, comprenhensive strength, water absorbtion, soluble salts....)

The Aqueduct in Skopje

- Position
- Known history and expected ages
- Sampling

The Aqueduct in Skopje

Position

- Macedonia – NE Skopje (village Vizbegovo)
- 380 m long, part of 10 km water-supply system
- 2 access ramparts, 53 pillars, 54 base vaults and 42 smaller vaults on the closed and open discharging openings above the pillars

The Aqueduct in Skopje

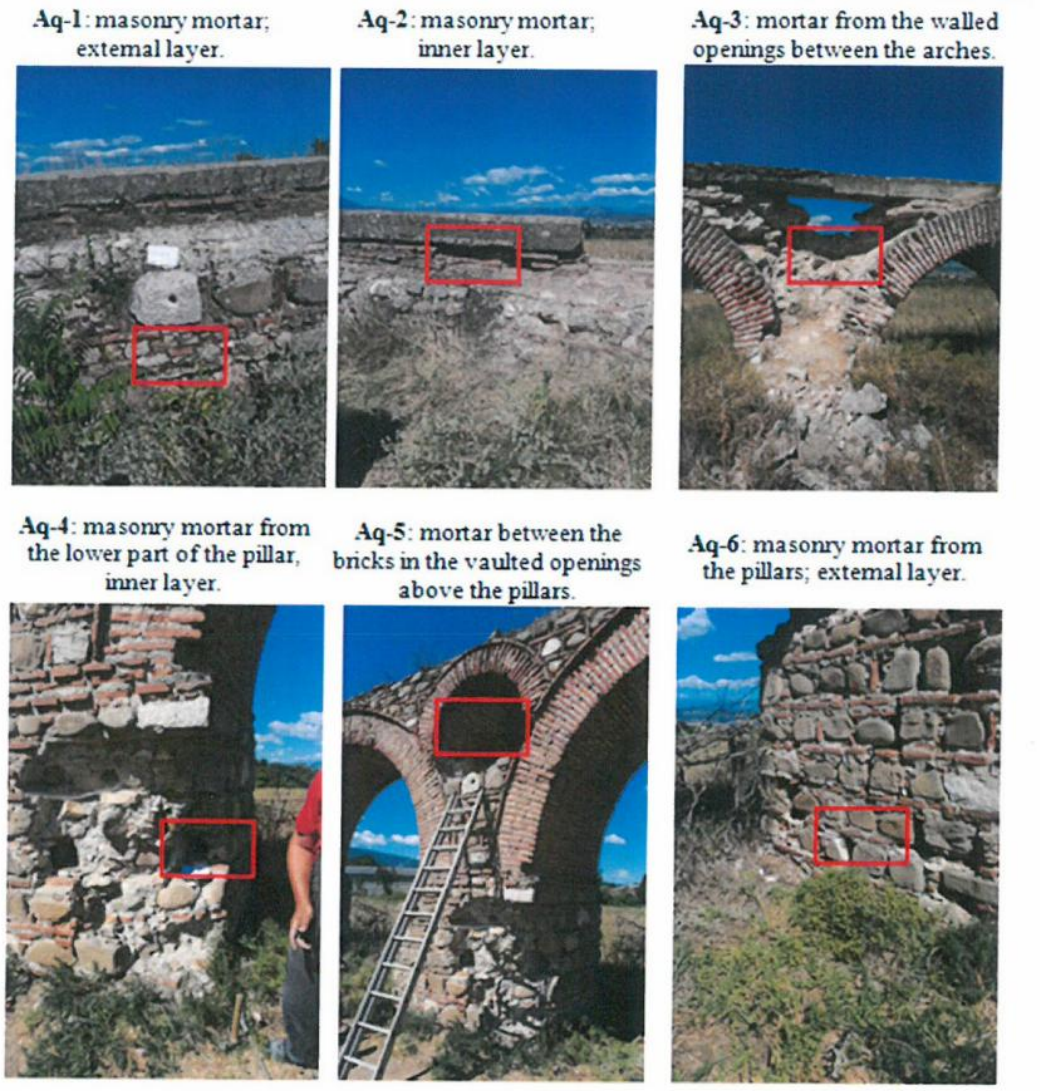
Known history and expected ages

- Reurbanization of Skopje by Byzantine emperor Justinian I (527 – 565 AD)
- Mustafa Pasha - 15th century
- Isa-Beg's water supply system - 16th century

The Aqueduct in Skopje

Sampling

- 6 positions – Aq1 to Aq6
- Cca 200 – 500 g of compact mortars



Experiment

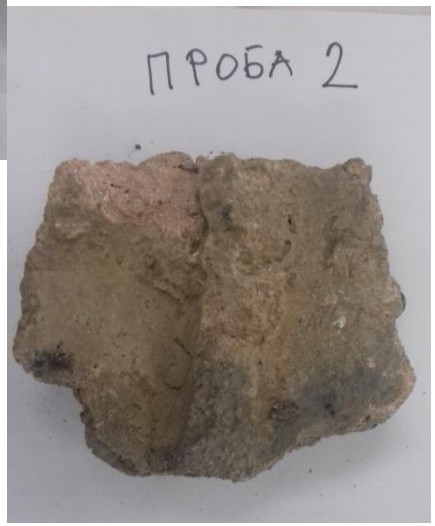
- Combine the Danish (Aarhus) and the Italian method:

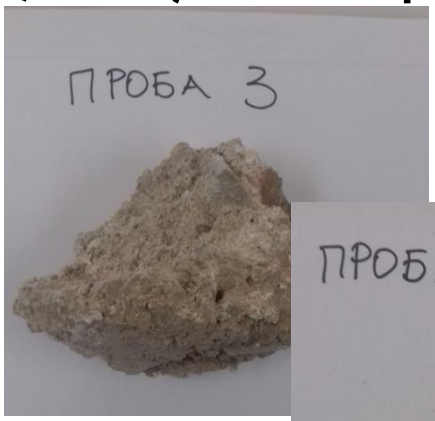
  CRYOSONIC separation (SUSPENSION part is the best)

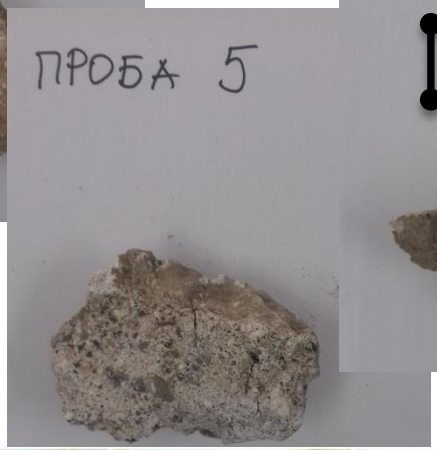
  + first CO_2 fractions

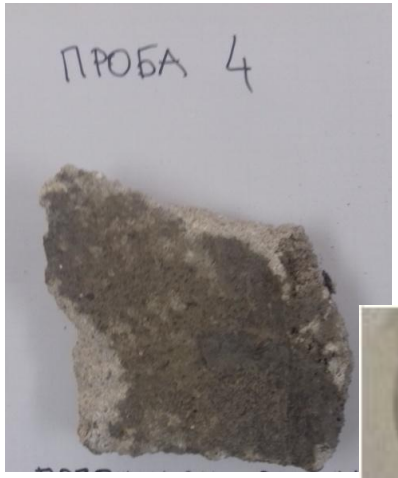
Experiment

- 6 samples of mortar, 10 – 15 g of bulk sample
- Measuring of pH (all 7, 7-8) - acceptable









Experiment

- CRYOSONIC separation

Subsampling from surface

Dipping into liq.nitrogen and in oven at 80 °C, alternately

Experiment

- CRYOSONIC separation

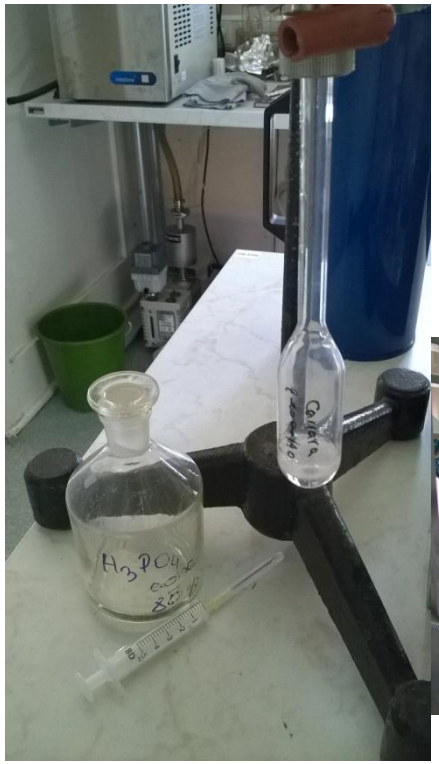
"Gentle" hammering

Wet sieving,
fractions **larger** than **450** μm – **TALOG, INKL;**
smaller than **450** μm - **LUMP** and **SUSP**

Experiment

- CRYOSONIC separation

Treating in ultrasonic bath, 30 minutes:
LUMP - fraction that sedimented
SUSP - fraction dispersed in water



Reaction with acid - CO_2 production:
SUSP1 - fraction of CO_2 produced within 60 s
SUSP2 - fraction of CO_2 produced after 60 s till the end of reaction

Experiment

- INCLUSION (>450 µm)

Experiment

- INCLUSION

Experiment – the structure

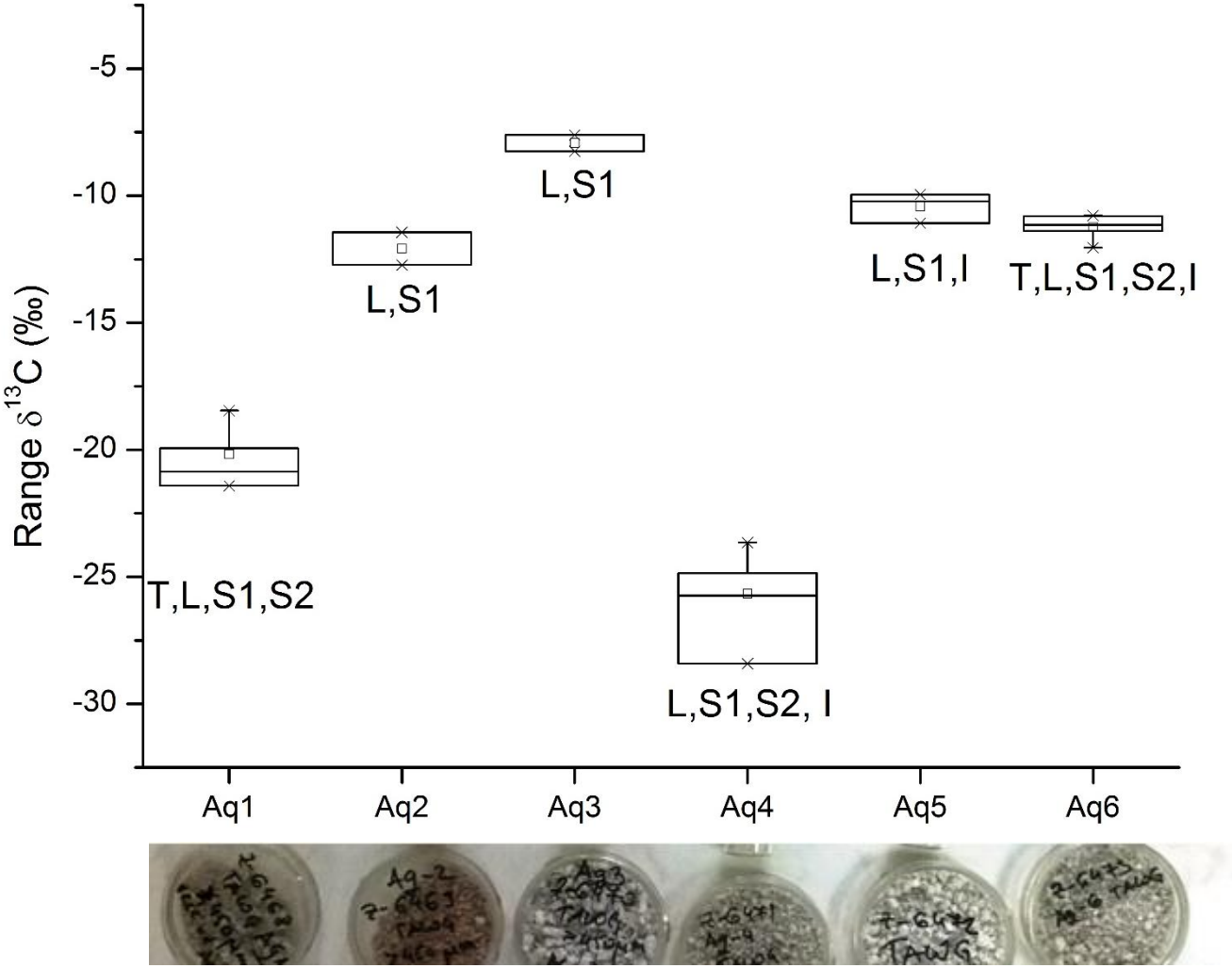
- Not all fractions were analyzed – prepared in CO_2 and graphite
- All: LUMP <->SUSP
- If avaible: INKL
- For the check: TALOG
- One Aq sample with all fractions

Experiment – How to chose the most plausible results?

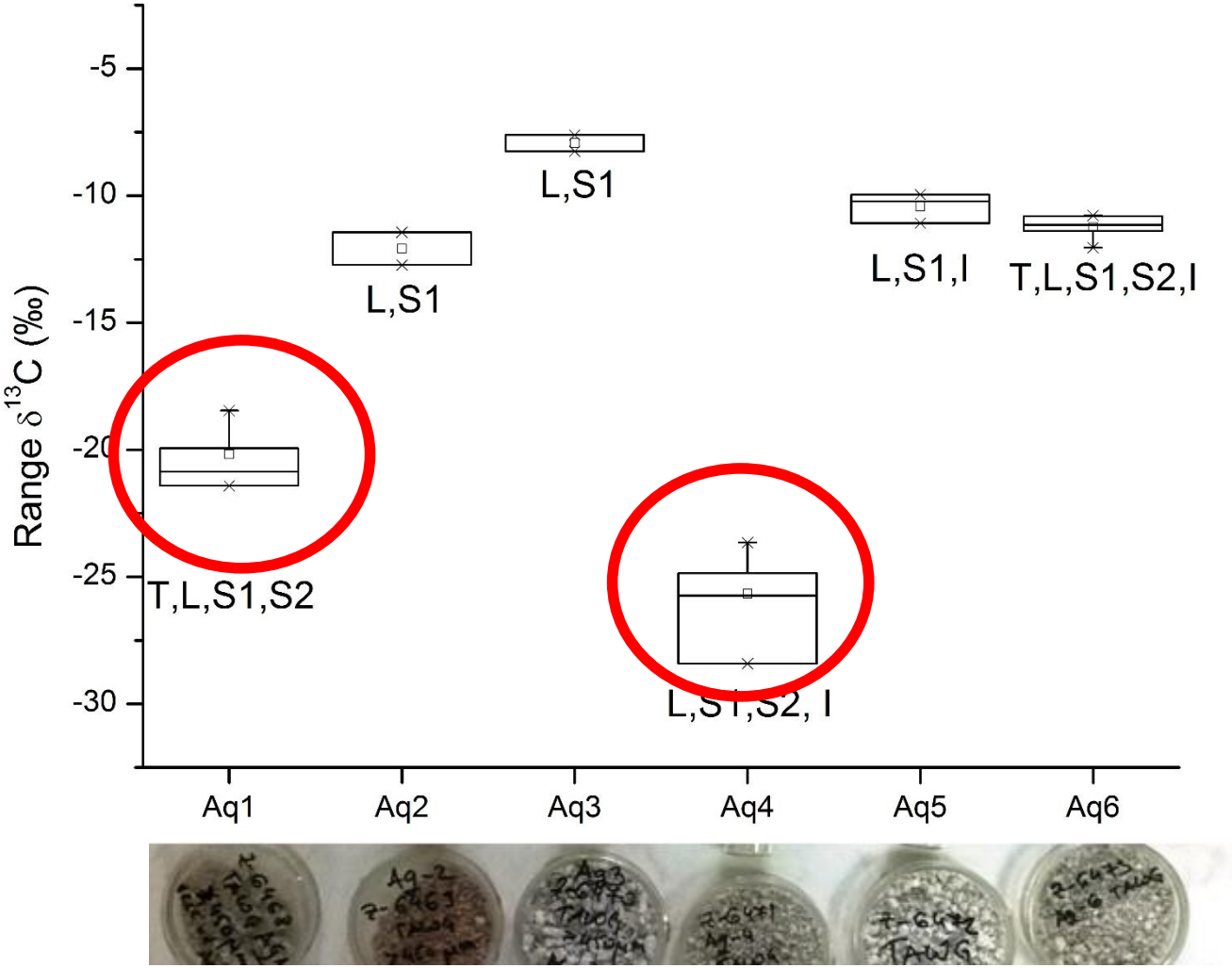
- We postulated that all the samples (Aq1-Aq6) were of the similar age
- What does ^{13}C tell us?
- INKL – the most reliable (no charcoal was found!)
- If "dead carbon" contamination exists line of age should be (from the oldest):

  TALOG > LUMP/SUSP2 > SUSP1=INCL

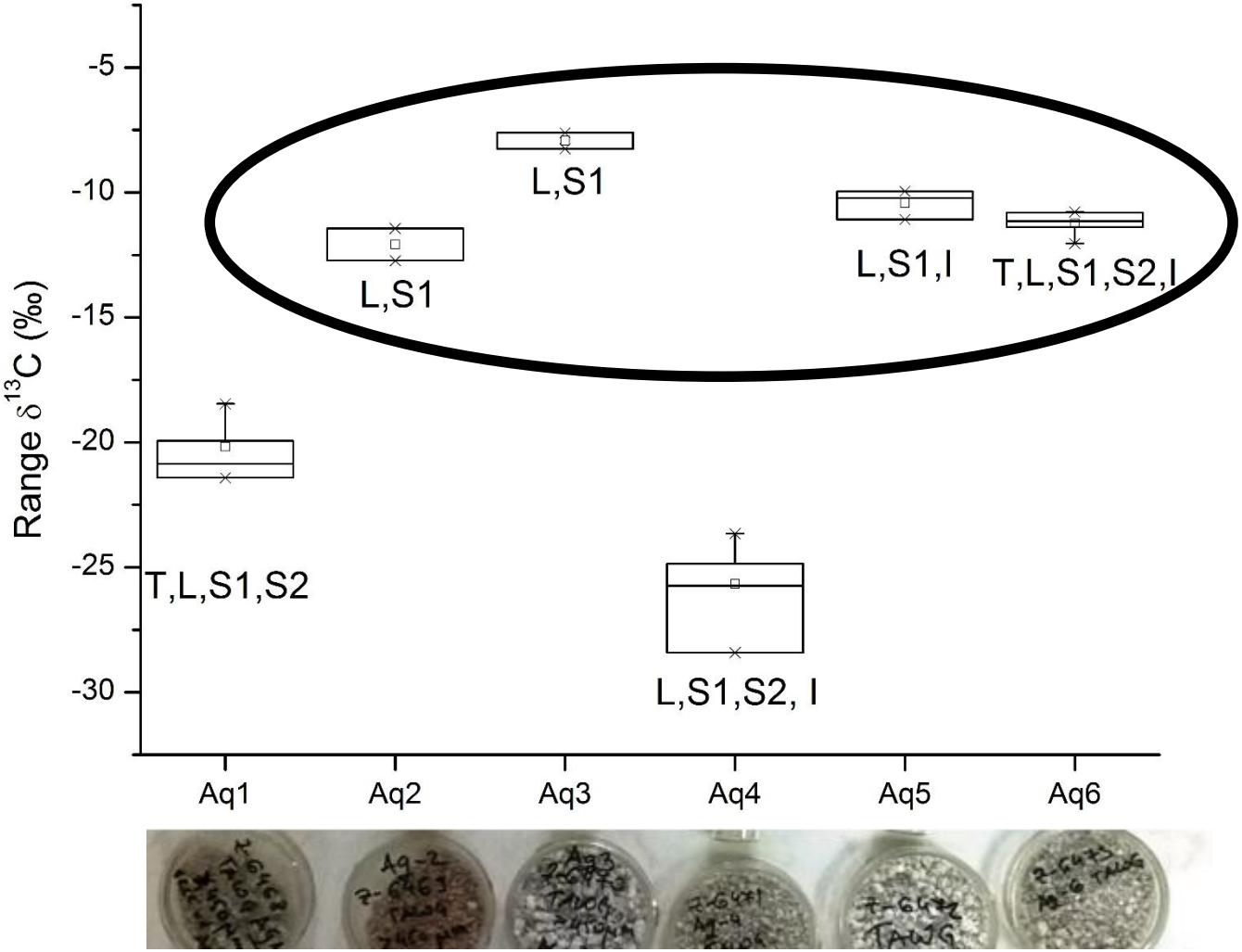
Results – first ^{13}C



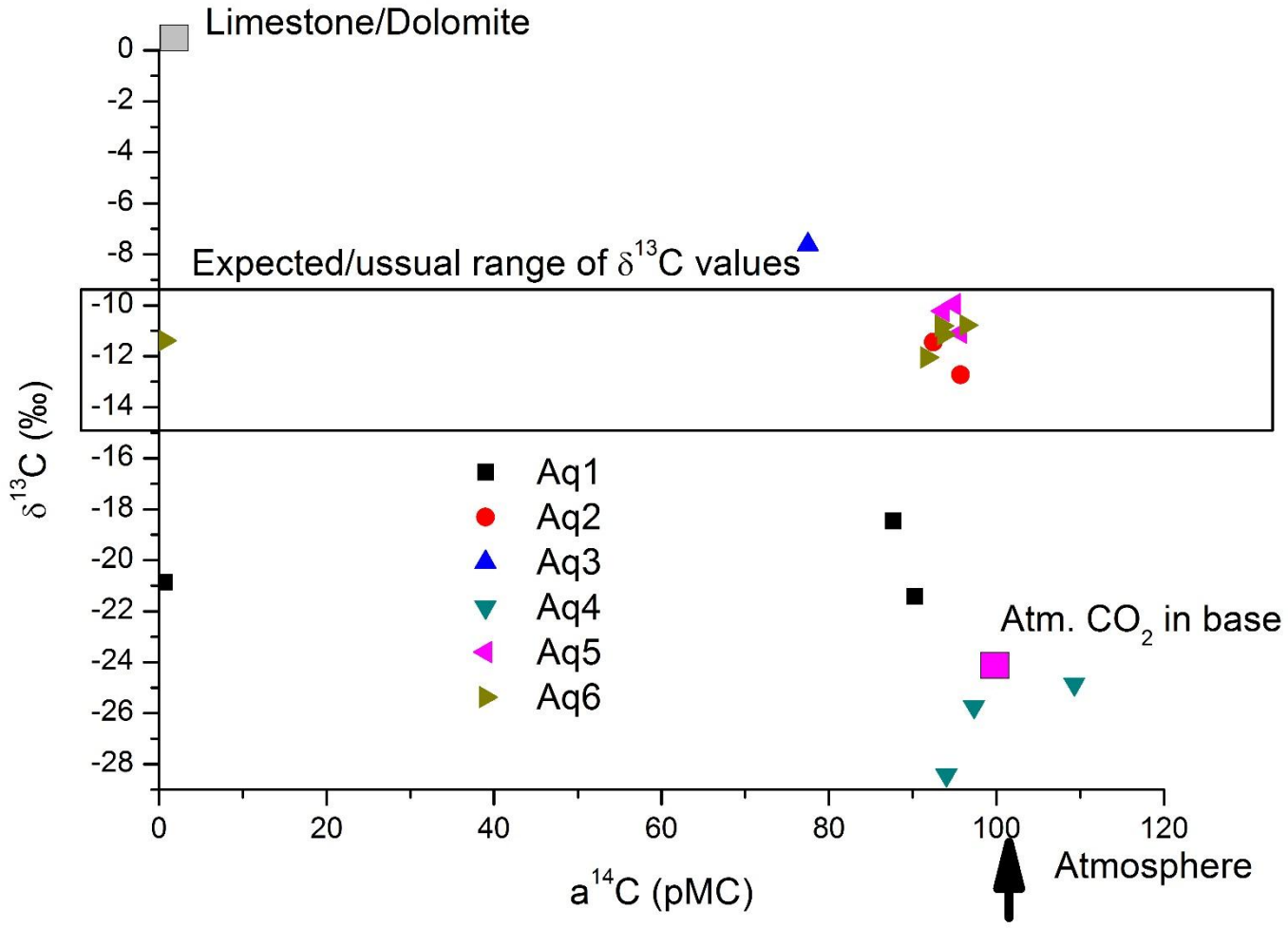
Results – first ^{13}C



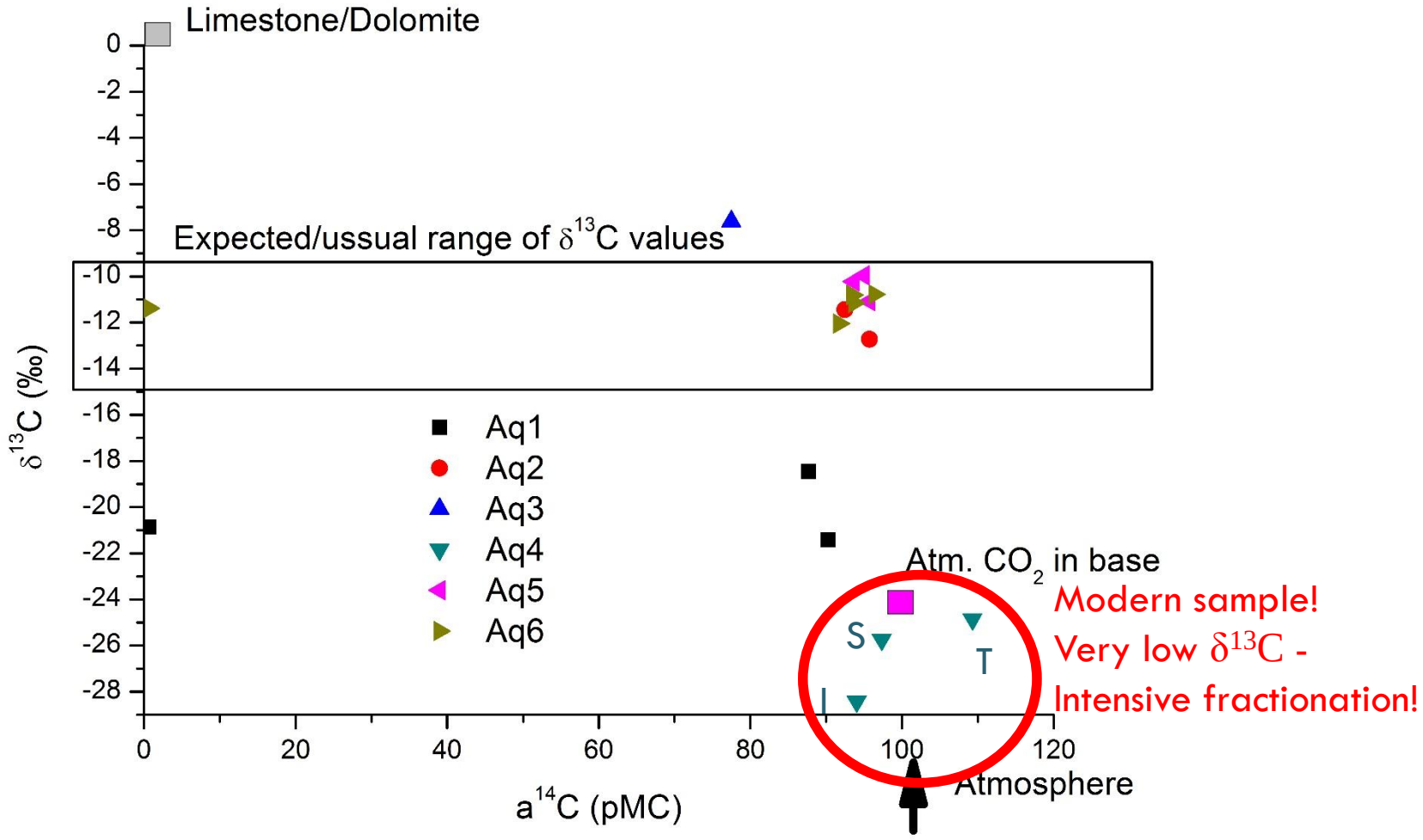
Results – first ^{13}C



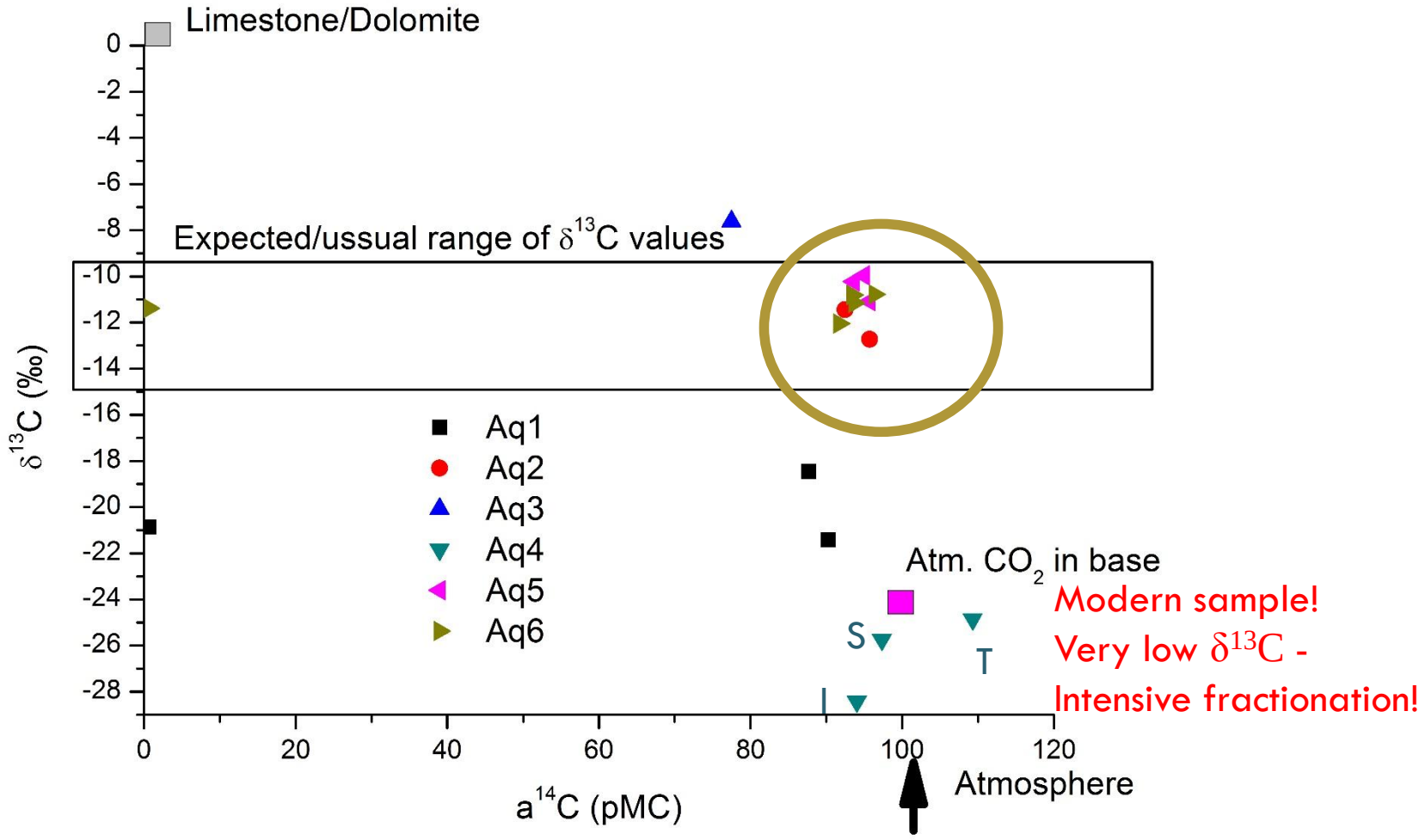
Results – ^{13}C and ^{14}C



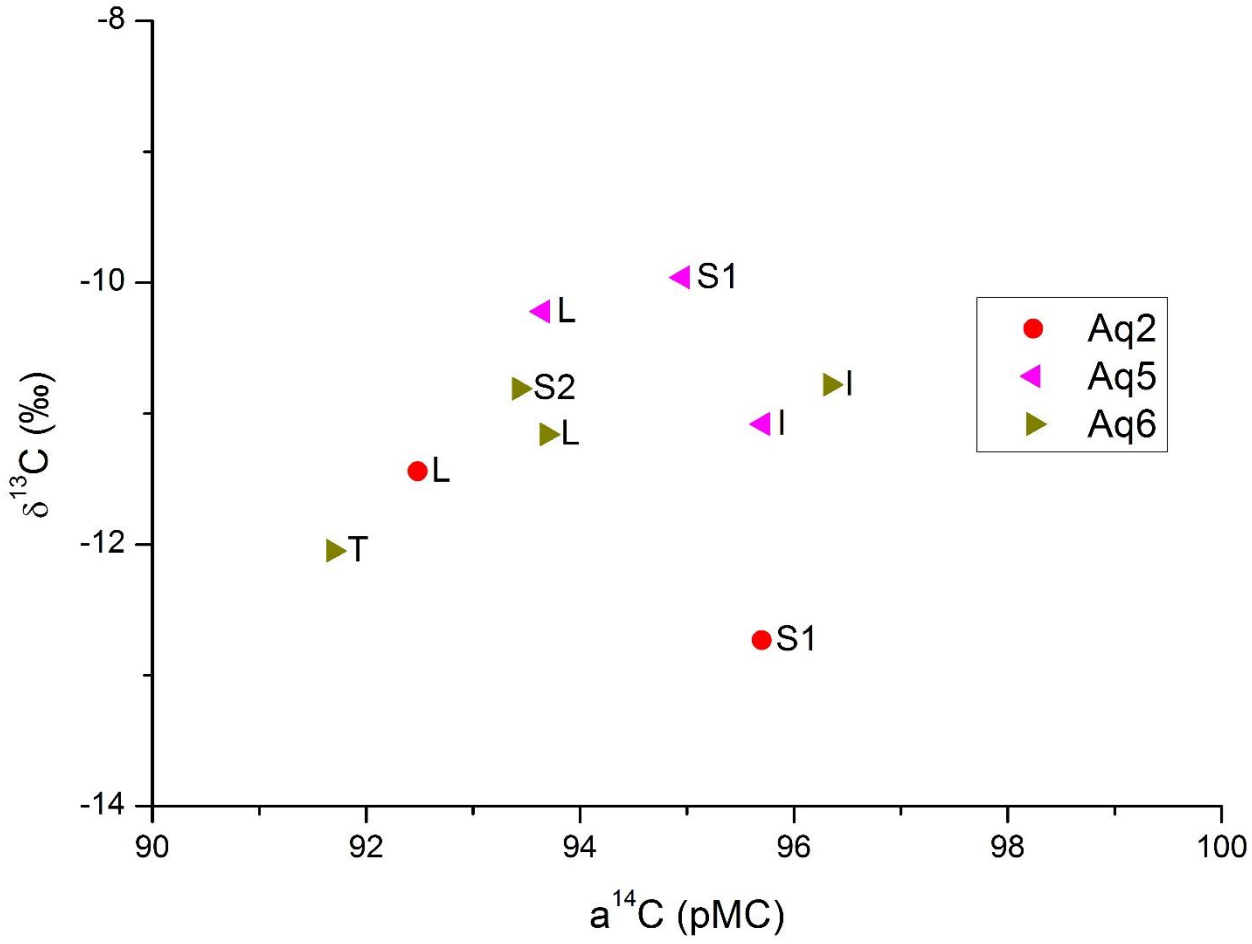
Results – ^{13}C and ^{14}C



Results – ^{13}C and ^{14}C

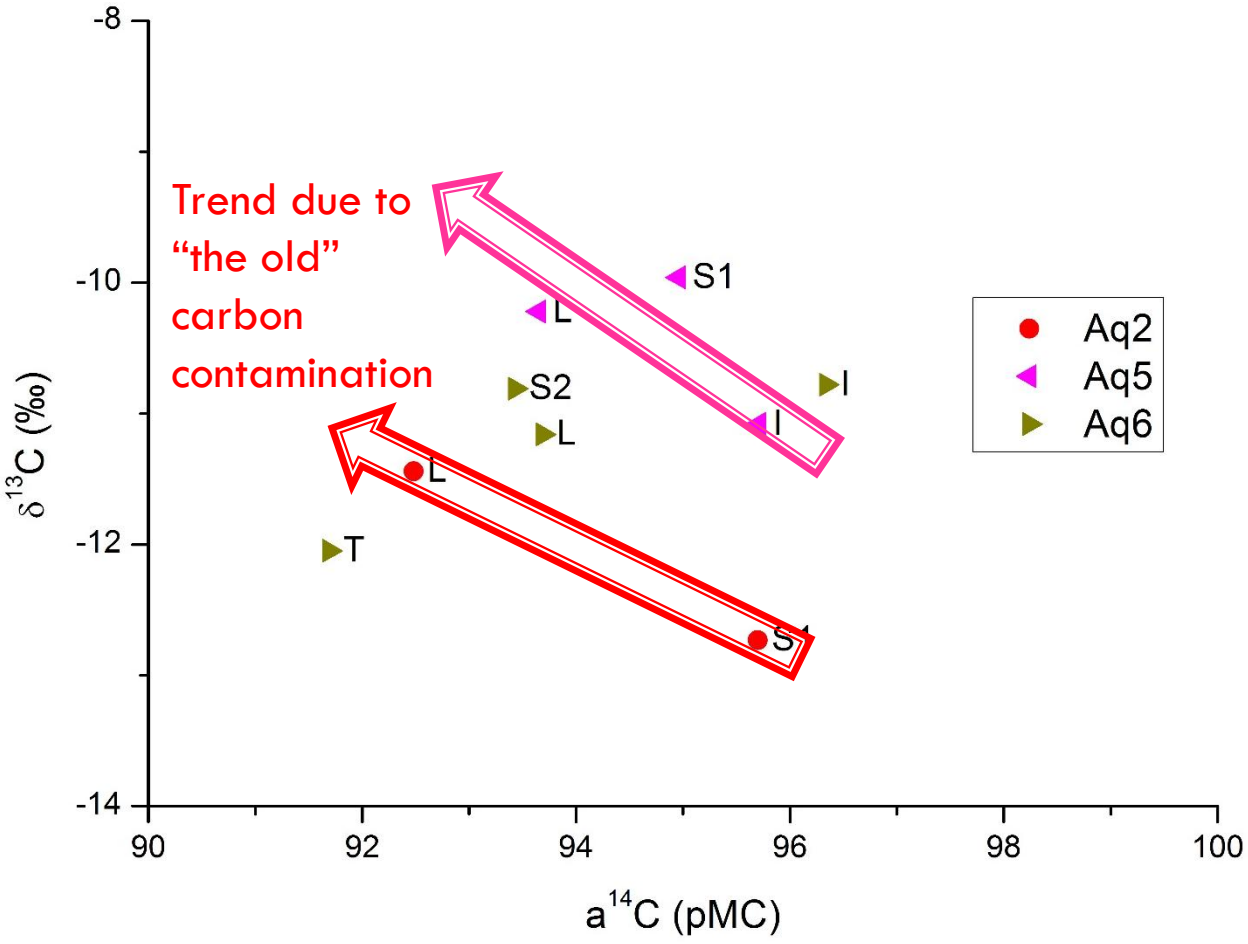


Results – ^{13}C and ^{14}C



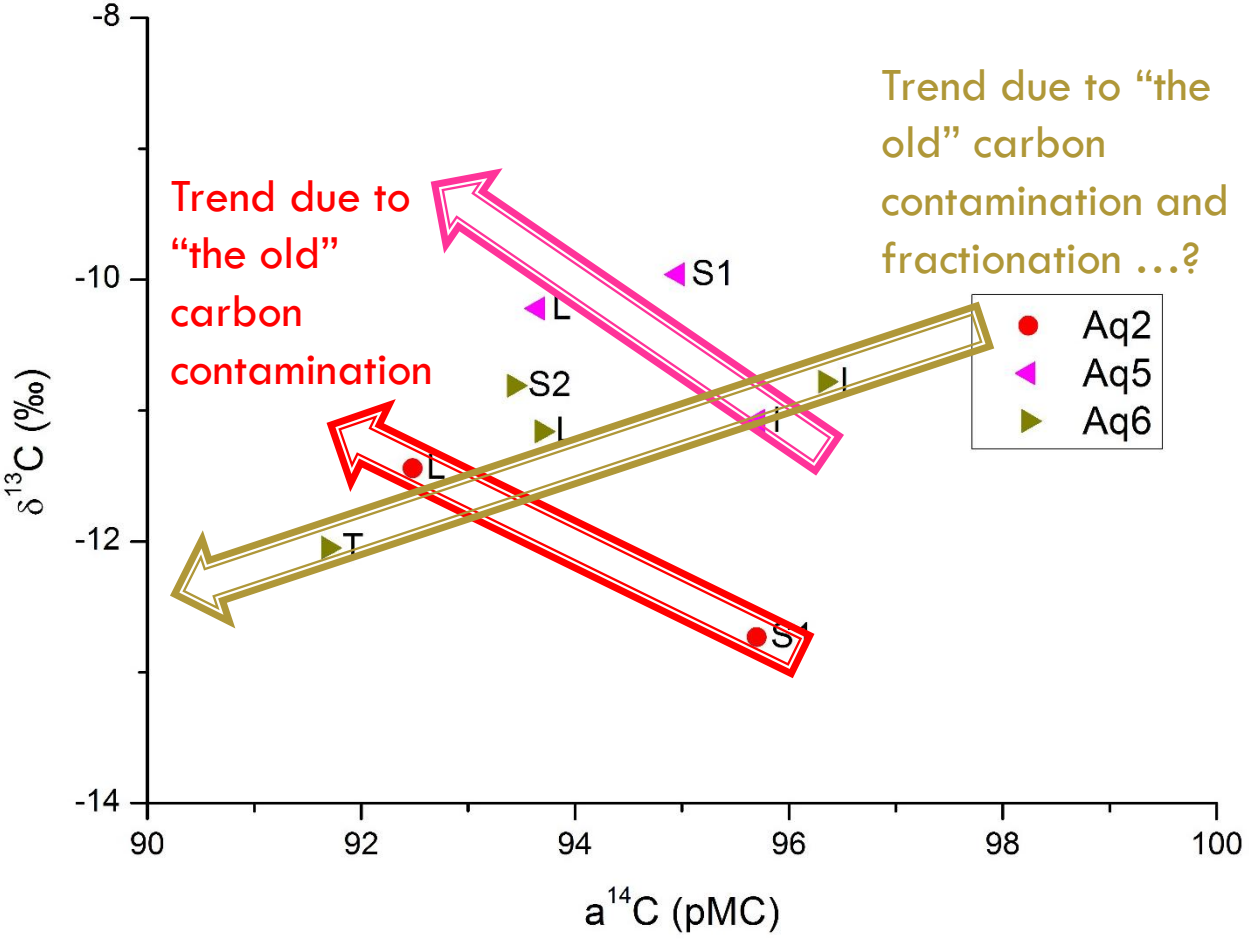
Suspended (S) fractions older than the inclusions (I)!

Results – ^{13}C and ^{14}C



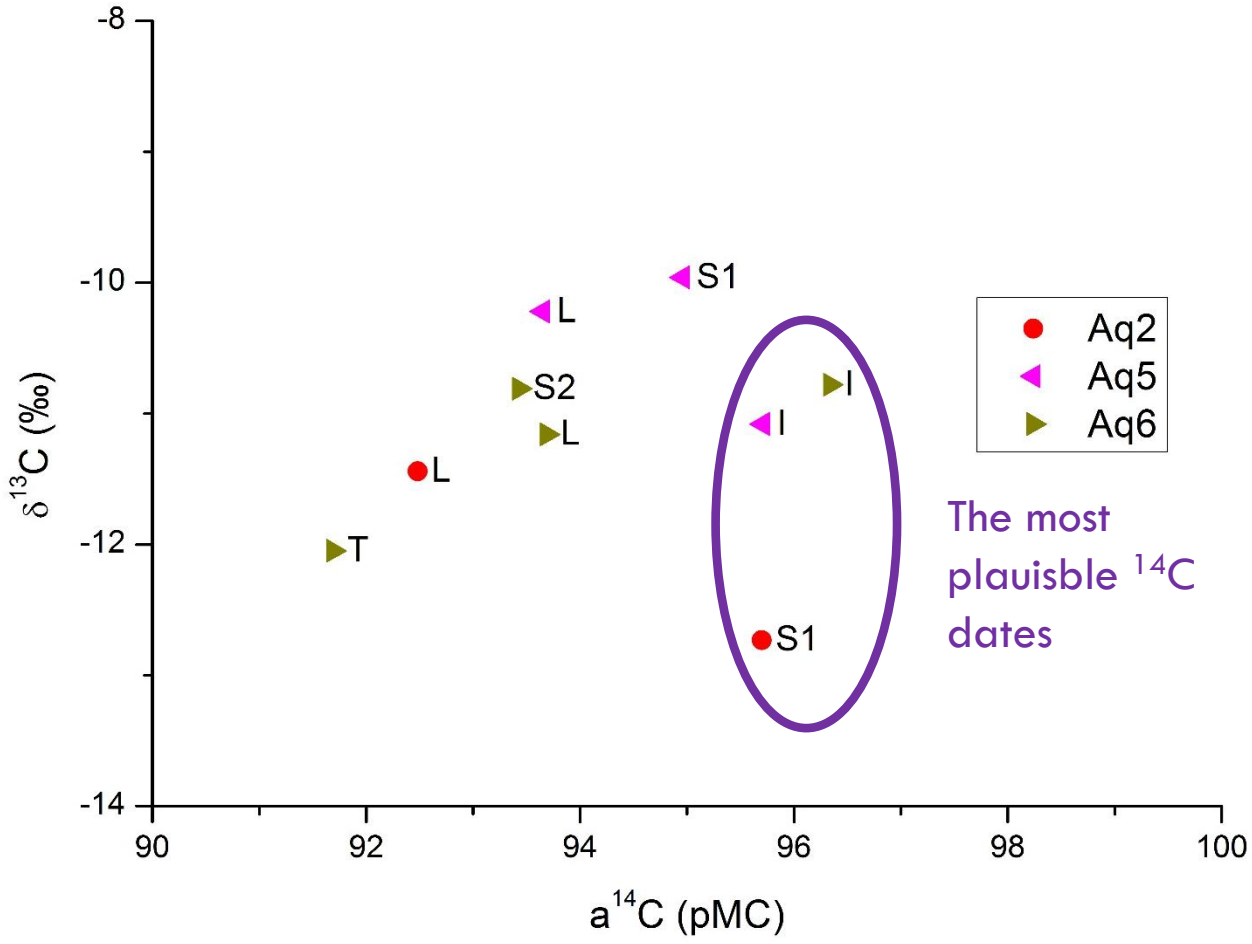
Suspended (S) fractions older than the inclusions (I)!

Results – ^{13}C and ^{14}C

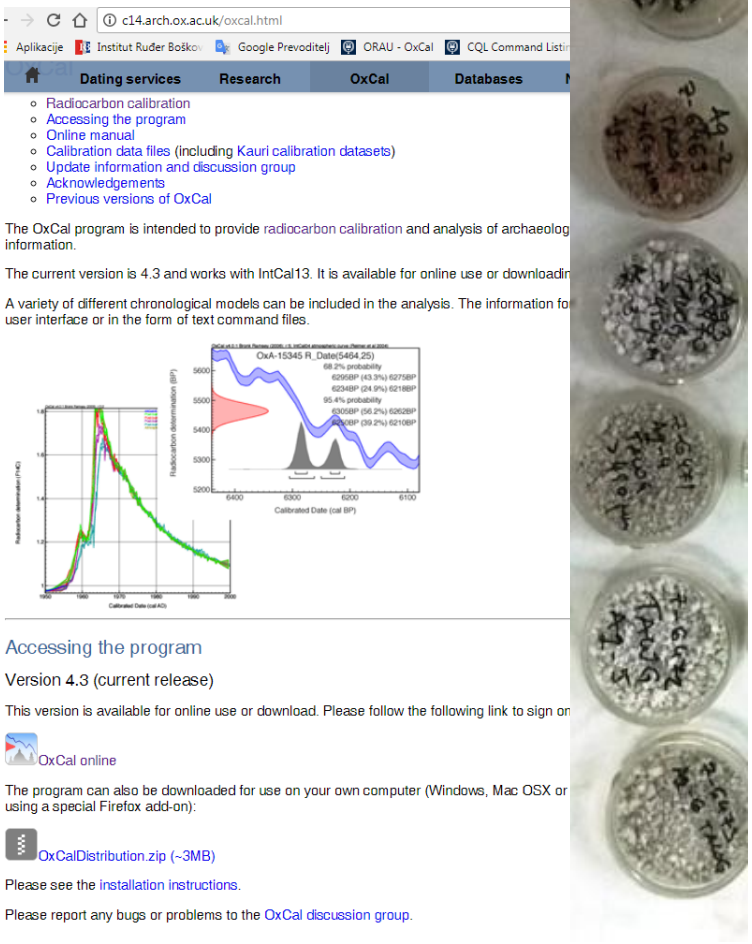


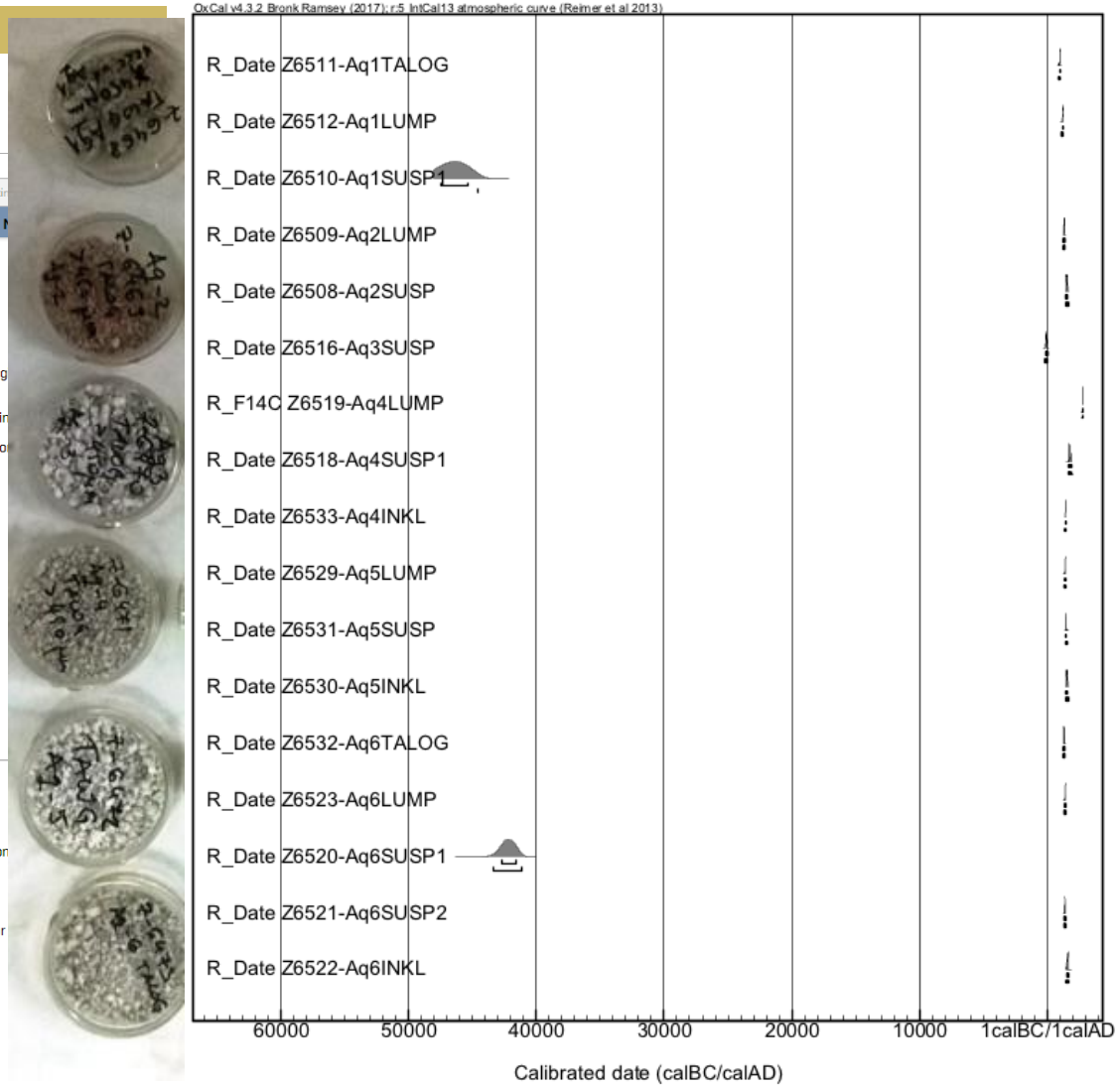
Suspended (S) fractions older than the inclusions (I)!

Results – ^{13}C and ^{14}C

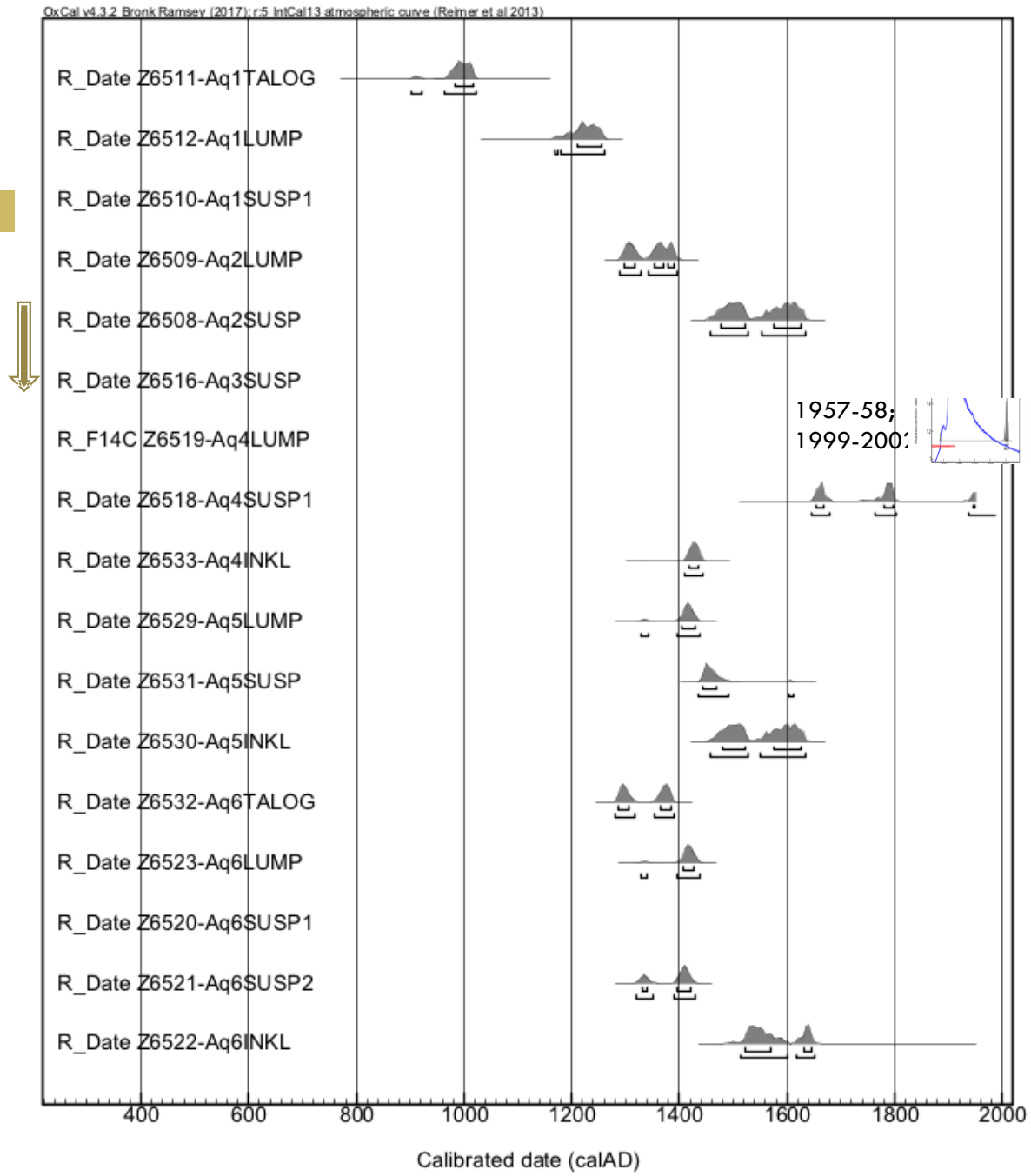


Results – ^{14}C age calibration

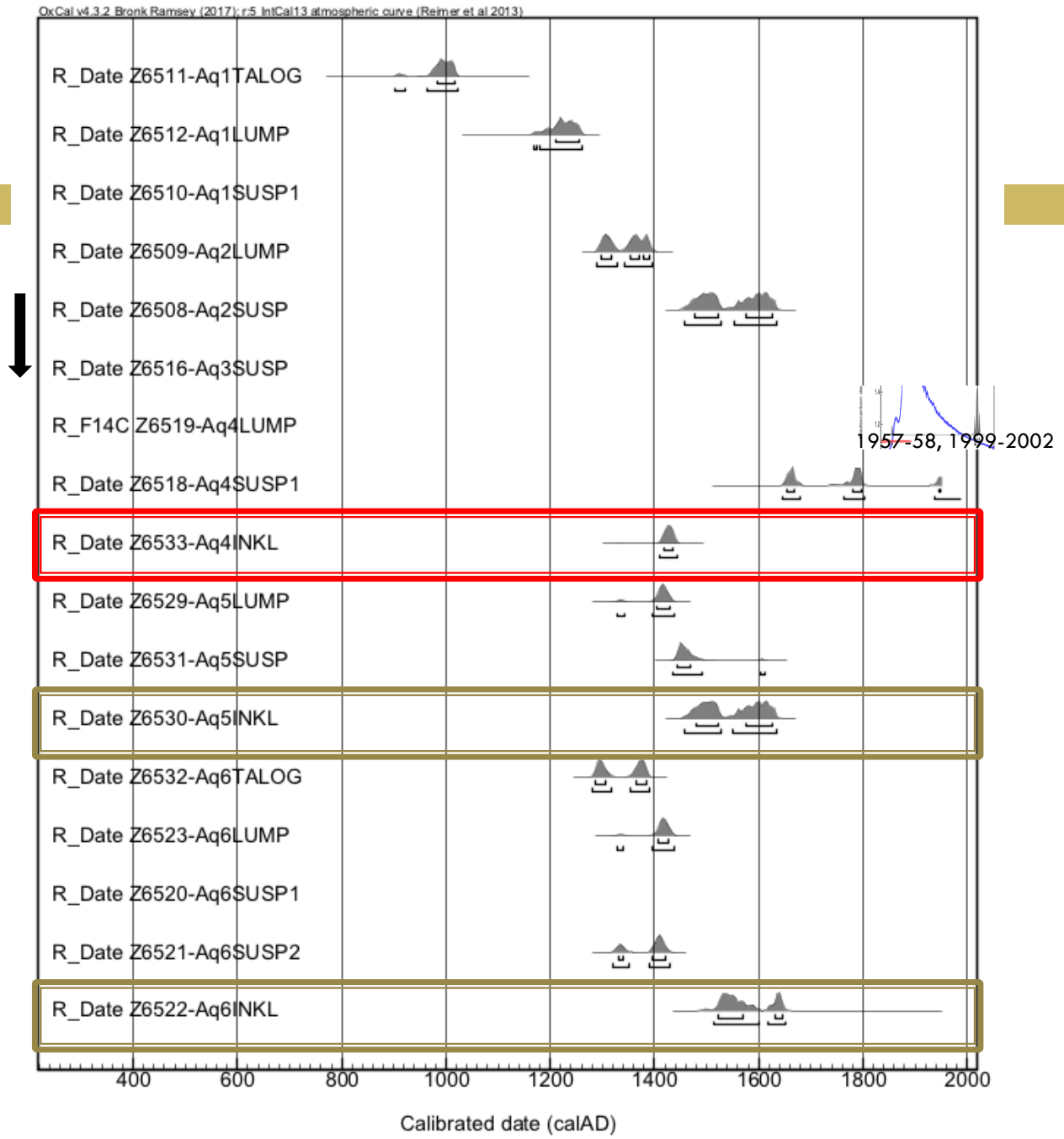




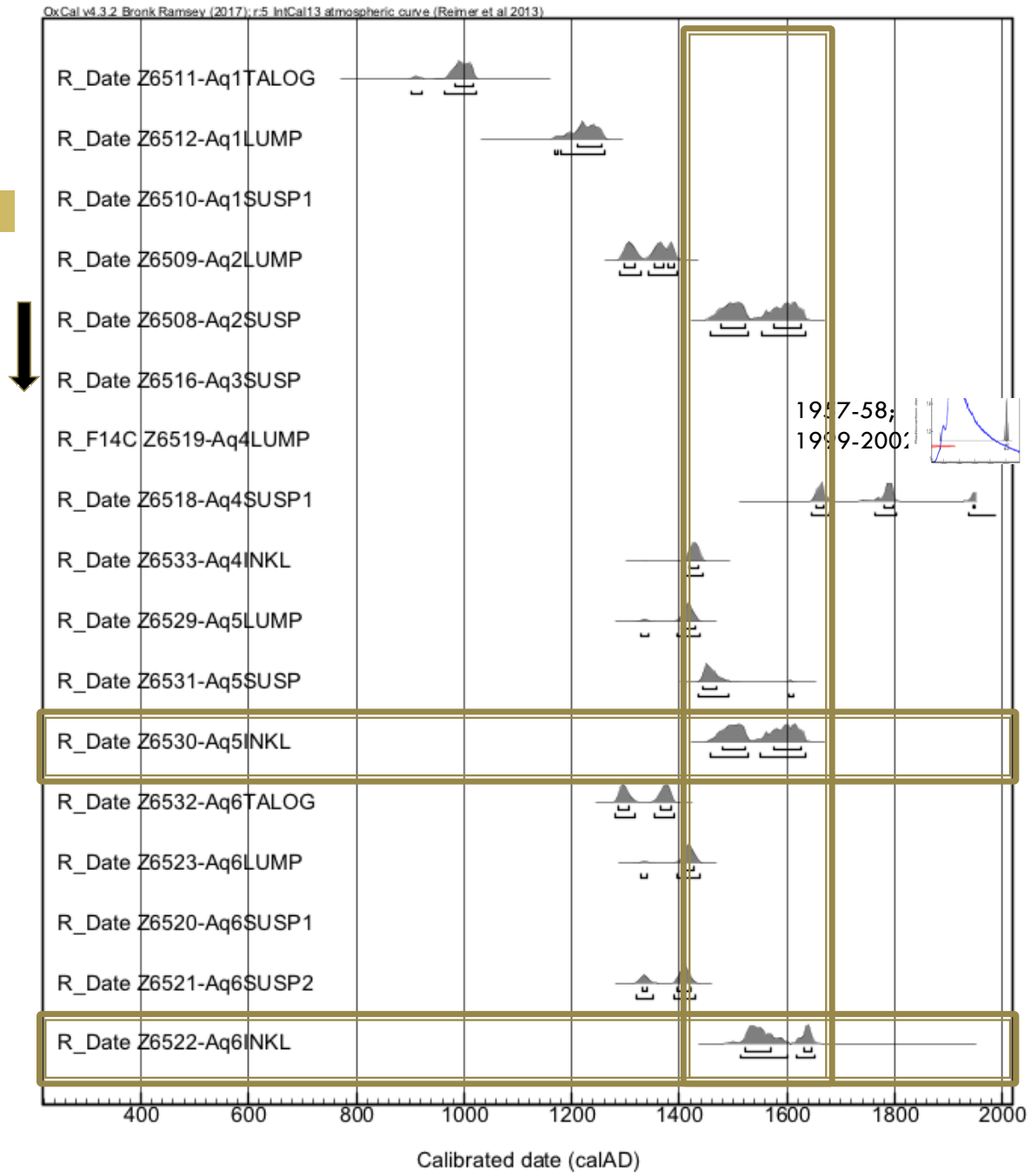
Results


OxCal v4.3.2 Bronk Ramsey (2017); r:5 IntCal13 atmospheric curve (Reimer et al 2013)
R_Date Z6511-Aq1TALOG
R_Date Z6512-Aq1LUMP
R_Date Z6510-Aq1SUSP1
R_Date Z6509-Aq2LUMP
R_Date Z6508-Aq2SUSP
R_Date Z6516-Aq3SUSP
R_F14C Z6519-Aq4LUMP
1957-58;
1999-200
R_Date Z6518-Aq4SUSP1
R_Date Z6533-Aq4INKL
R_Date Z6529-Aq5LUMP
R_Date Z6531-Aq5SUSP
R_Date Z6530-Aq5INKL
R_Date Z6532-Aq6TALOG
R_Date Z6523-Aq6LUMP
R_Date Z6520-Aq6SUSP1
R_Date Z6521-Aq6SUSP2
R_Date Z6522-Aq6INKL
400
600
800
1000
1200
1400
1600
1800
2000
Calibrated date (calAD)

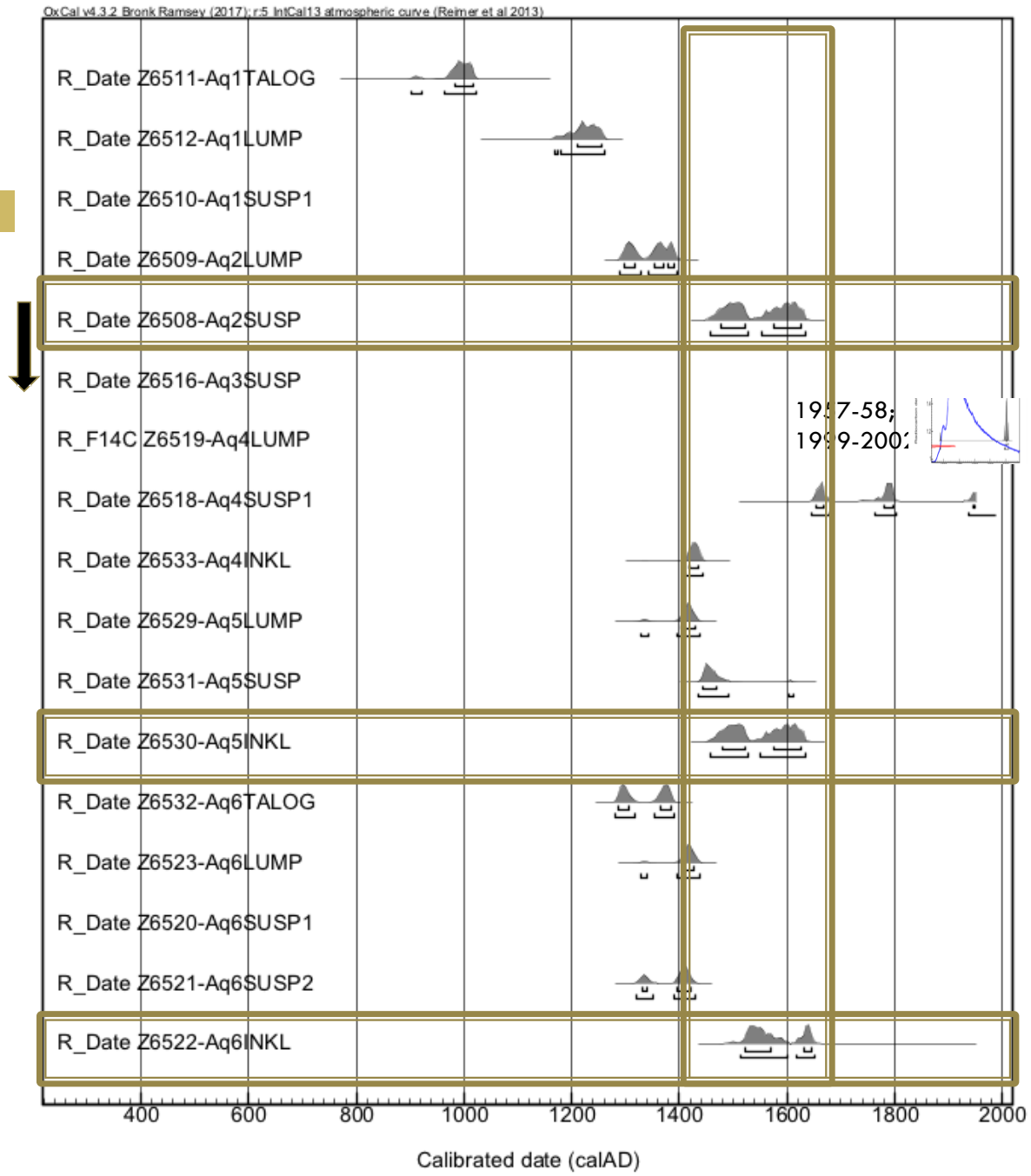
Discussion


OxCal v4.3.2 Bronk Ramsey (2017); r:5 IntCal13 atmospheric curve (Reimer et al 2013)
R_Date Z6511-Aq1TALOG
R_Date Z6512-Aq1LUMP
R_Date Z6510-Aq1SUSP1
R_Date Z6509-Aq2LUMP
R_Date Z6508-Aq2SUSP
R_Date Z6516-Aq3SUSP
R_F14C Z6519-Aq4LUMP
R_Date Z6518-Aq4SUSP1
R_Date Z6533-Aq4INKL
R_Date Z6529-Aq5LUMP
R_Date Z6531-Aq5SUSP
R_Date Z6530-Aq5INKL
R_Date Z6532-Aq6TALOG
R_Date Z6523-Aq6LUMP
R_Date Z6520-Aq6SUSP1
R_Date Z6521-Aq6SUSP2
R_Date Z6522-Aq6INKL
1957-58, 1999-2002
400
600
800
1000
1200
1400
1600
1800
2000
Calibrated date (calAD)

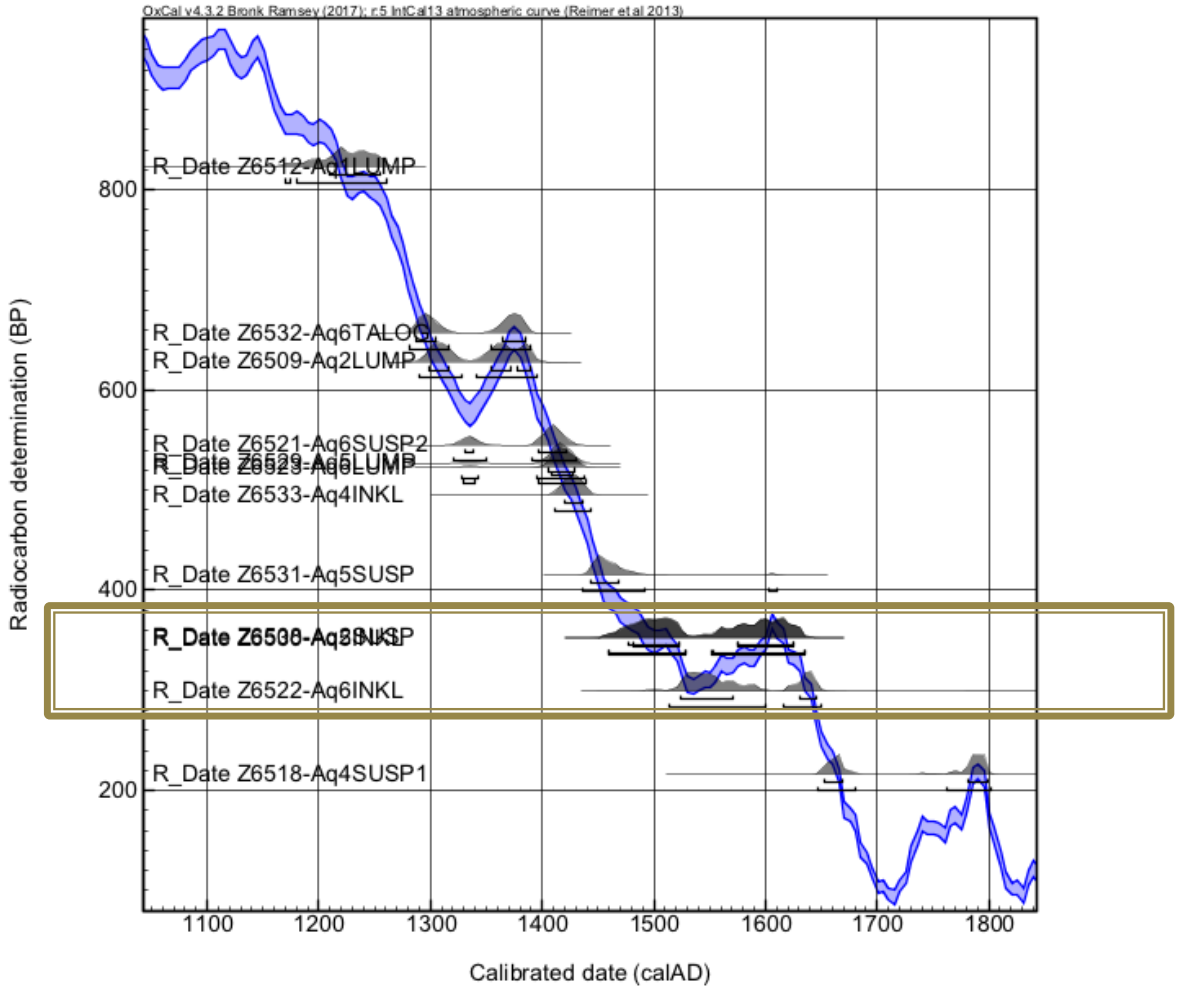
Discussion


OxCal v4.3.2 Bronk Ramsey (2017); r:5 IntCal13 atmospheric curve (Reimer et al 2013)
R_Date Z6511-Aq1TALOG
R_Date Z6512-Aq1LUMP
R_Date Z6510-Aq1SUSP1
R_Date Z6509-Aq2LUMP
R_Date Z6508-Aq2SUSP
R_Date Z6516-Aq3SUSP
R_F14C Z6519-Aq4LUMP
R_Date Z6518-Aq4SUSP1
R_Date Z6533-Aq4INKL
R_Date Z6529-Aq5LUMP
R_Date Z6531-Aq5SUSP
R_Date Z6530-Aq5INKL
R_Date Z6532-Aq6TALOG
R_Date Z6523-Aq6LUMP
R_Date Z6520-Aq6SUSP1
R_Date Z6521-Aq6SUSP2
R_Date Z6522-Aq6INKL
400
600
800
1000
1200
1400
1600
1800
2000
Calibrated date (calAD)

Discussion


OxCal v4.3.2 Bronk Ramsey (2017); r:5 IntCal13 atmospheric curve (Reimer et al 2013)
R_Date Z6511-Aq1TALOG
R_Date Z6512-Aq1LUMP
R_Date Z6510-Aq1SUSP1
R_Date Z6509-Aq2LUMP
R_Date Z6508-Aq2SUSP
R_Date Z6516-Aq3SUSP
R_F14C Z6519-Aq4LUMP
R_Date Z6518-Aq4SUSP1
R_Date Z6533-Aq4INKL
R_Date Z6529-Aq5LUMP
R_Date Z6531-Aq5SUSP
R_Date Z6530-Aq5INKL
R_Date Z6532-Aq6TALOG
R_Date Z6523-Aq6LUMP
R_Date Z6520-Aq6SUSP1
R_Date Z6521-Aq6SUSP2
R_Date Z6522-Aq6INKL
400
600
800
1000
1200
1400
1600
1800
2000
Calibrated date (calAD)

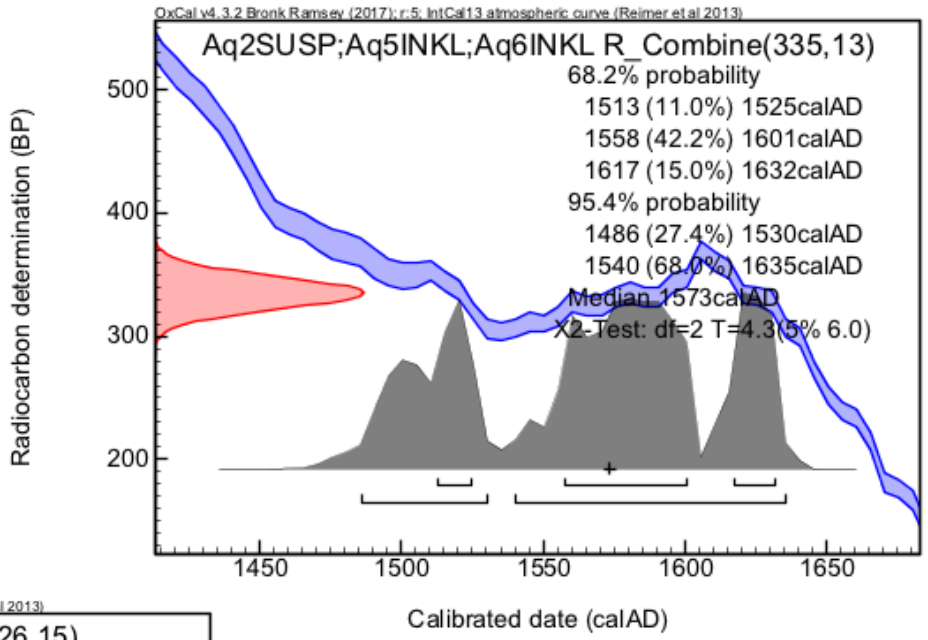
Discussion

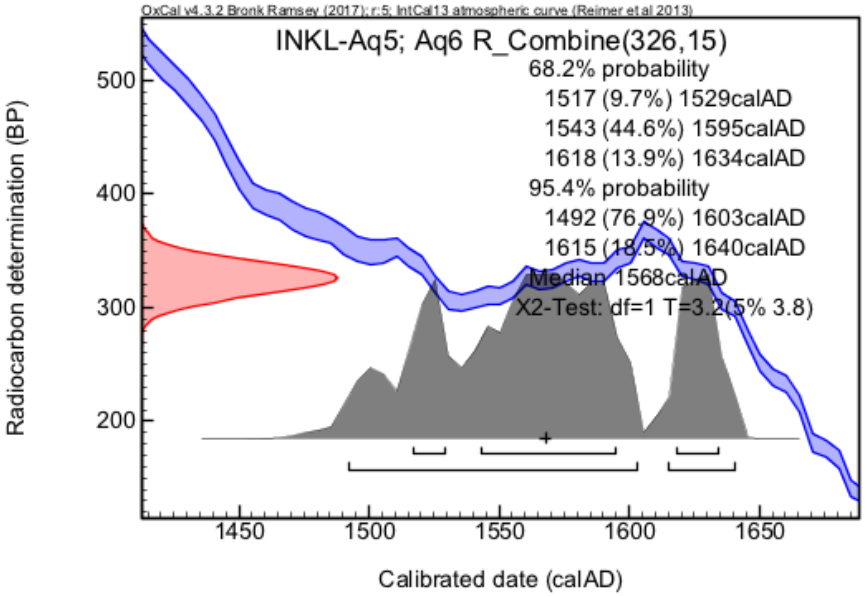

OxCal v4.3.2 Bronk Ramsey (2017); r:5 IntCal13 atmospheric curve (Reimer et al 2013)
R_Date Z6512-Aq1LUMP
R_Date Z6532-Aq6TALOG
R_Date Z6509-Aq2LUMP
R_Date Z6521-Aq6SUSP2
R_Date Z6533-Aq4INKL
R_Date Z6531-Aq5SUSP
R_Date Z6522-Aq6INKL
R_Date Z6518-Aq4SUSP1
800
600
400
200
1100
1200
1300
1400
1500
1600
1700
1800
Radiocarbon determination (BP)
Calibrated date (calAD)

Discussion

Data combining…

Chi. square test, 5%





Most plausable age of Aqueduct construction is15 - 17 cet.

Conclusions

- In dating use more samples of the same object
- $\delta^{13}C$ points to the reliability of the radiocarbon results
- Inclusions are a good material, but need to be compared to the other fractions
- CRYOSONIC method **did not yield reliable results** (SUSP from 40 000 BP to modern, one sample even true!)
- The issue persists: “It works!... Unless, it doesn’t…”

Conclusions

The most plausible date of the Aqueduct is during Mustafa Pasha or Isa-Beg (15-16 cent.).

(even if we had charcoal, that would be the most precise result, since the calibration curve is quite flat in that time period)

And the Byzantine times can be ruled out!

Aknowledgment

- **Executive project design for conservation and restauration of the Aqueduct in Skopje (2014)**
- Thank you for your attention!