Zircon digestion (05/2017)

IMPORTANT:

- **only start if you got a theoretical and practical introduction into HF handling and security**
- **if you are not fealing save or familiar with the method and safety do not start working**

Composition of zircon (U-Th)/He spike:

5.208 ng/g nominally pure 233-U
5.346 ng/g nominally pure 230-Th

Required materials

1. Four teflon liner, should be in Room 202 next to one of the heating plates, they do not have numbers compared to those from the Geochemistry
2. Teflon tweezers are below the fume hood next to the window in Room 202
3. Five teflon trays are in a box below the fume hood next to the window in Room 202
4. PFA vials and lids are next to or on the hot plate in Room 202
5. U-Th spike, is in the fridge in Room 201A
6. Pipette and pipette tips are in Room 202
7. Four bombs are in Room 201C. Our bombs are labelled (5852, 5853, 5880, 5881) and should be on or next to the oven.
8. HF/HNO_3 are located under the fume hood next to the window in Room 202. 7:1 HF-HNO_3, pure HF and pure HNO_3 (distilled acids from clean lab).
9. Fine tweezers from picking lab to handle capsules

Set up HF + HNO_3 bomb **Mon / Tue / Wed**

1. Open teflon liner, discard HCl, drop liner in beaker with H_2O to clean; dry under red light
2. Take PFA vials out of storage container bottles and place into tray:
pour off H_2O, pour vials and lids into lids of storage container, with tweezers take vials, shake out water drops, place into tray
3. Dry under red light for >1h
4. Place vials and lids on Al foil to let them cool and to reduce static charging
Add 100 µl spike by pipette and weight
5. Add zircon capsules, take capsules out of sample container, put on weighting paper and use tweezer to put into vial
6. Carefully dry spike at 75°C and red light with lids off (~2 h)
Do not let vials sit on the hot plate once they are dry. Samples in the middle of the tray will likely dry faster.
7. With pipette add 200 µl conc. HF + 50 µl conc. HNO_3, use acids from new clean lab. Add first the weak acid (HF) and afterwards HNO_3 drop by drop.
8. With tweezers place vials into tree. Make sure that the position of samples in the tree is unambiguously recorded (e.g. tree discs are marked by a little notch). Add 6 ml conc. HF to liner. The resulting acid has 43% HF and 6.5% HNO_3 (7:1)
9. Place tree in liner, close lid
10. Place liner into bomb. Make sure the floor plate is in the bomb. Put a paper with the special black/white tool in the fume hood. Place the bomb on it. It will move the floor plate up to facilitate easy insertion of the liner. Insert first the liner, then the aluminium lid and afterwards the small iron lid. Move the bump out of the special tool and close it with the large lid. Close the bomb with a torque wench at 22 lb. Place bomb in heater and heat for 5 days at 200°C.

Set up HCl bomb Mon

11. Let bomb cool for 3-4 h, open bomb and take out liner.
You can save time by switching off the oven Sunday night, leave door closed. Clean liner from outside with paper in Room 201. Use large rubber gloves to open liner (they are located in one of the drawer below the sink).
12. If liner doesn't open (usual), reheat under red light and 80°C for 20 min. Open liner in fume hood next to the door in Room 201C. Careful HF/HNO_3 gases will be released. Led it cool for a while.
13. Move vials from tree to tray. Carefully dry at 75°C and red light with lids off (~2-3 h). Do not let vials sit on the hot plate once they are dry. If drying overnight is necessary, close lids and switch off heat.
14. Rinse liner with H_2O and put tree into beaker with H_2O to clean.
15. Add 100 µl 6M HCl to each vial and 7 ml 6M HCl to liner.
16. Rebomb 24 h at 200°C.

Transform chlorides into nitrides **Wed**

(The day before measurement; samples can be stored in HCl in sealed liners in clean lab if needed)
17. Open bomb.
18. Carefully dry samples with lids off.
19. For final acid concentration of 5% HNO_3 + 0.5% HF dissolve sample in HNO_3+HF concentrate mix, dilute with H_2O, and add 5% HNO_3-HF mix to obtain a final volume of 3 ml.
20. Prepare mix of conc. HNO_3 + HF (7:1), e.g., 21 ml 65% HNO_3 + 3 ml 48% HF for 120 vials
21. Add 190 µl acid mix to each vial, close lid, and let sit over night (alternatively, heat carefully at 50°C for ~1 h or until salts are dissolved).
22. Next day, prepare 5% HNO_3 + 0.5% HF (1 liter bottle in new clean lab). Fill each autosampler vial with 4 ml 5% HNO_3 + 0.5% HF and 1.8 ml H_2O (premix or add individually). Transfer sample solution into autosampler vial and rinse the sample vial with 193 µl H_2O. Transfer it to the autosampler vial and place it into the autosampler box under the fume. (Solution in autosampler vial have 190 µl conc. HF/HNO_3 + 1993 µl H_2O = 2.183 ml 5% HNO_3 + 0.5% HF + 4 ml 5% HNO_3 + 0.5% HF = 6.183 ml 5% HNO_3 + 0.5% HF)
23. Cover the vials with parafilm and use a box to transport the samples to the I-CAP.

Run samples **Thu**

24. Bring USB key with sample list
25. Prepare dummy, acid blank and ZirconJuice in three pre-cleaned 65 ml PP vials (or use old ones)
26. Prepare calibration solutions in pre-cleaned autosampler vials
27. Fill-up 5l container with washing agent
28. After completion of the ICP measurements store remaining sample solution as primer for next ICP session

Calibration solutions

Stock: ~10 ppm Zr
Kal3 (1000 ppb): 1.8 g Zr-10ppm + 14 g 5% HNO_3 + 0.5 HF
Kal2 (500 ppb): 0.9 g Zr-10ppm + 15 g 5% HNO_3 + 0.5 HF
Kal1 (60 ppb): 0.9 g Zr-1000ppb + 15 g 5% HNO_3 + 0.5 HF

ICP measurements

1. make sure the machine is running
2. start PC if not running and open programs ‚Instrument control' and ‚Qtegra' (on desktop) if not running
3. open water for cooling (two screw valves at the wall behind the I-CAP)
4. change sample introduction system (teflon spray chamber and needle with thin plastic tube)
5. open plasma chamber and change sample cone, skimmer cone and extraction lens with special

screwdriver, for apatite a high sensitivity is required and for zircon a good matrix (cones are the same for ap/zr but there are two extraction lenses, one for ap and one for zr)

6. fill up the washing agent (~5 l 5% HNO3 + 0.5% HF); bottle with washing agent should be placed after usage in a fume cupboard
7. put tubes on peristaltic pump, rotating away from the machine (make sure the transport direction is correct)
8. put large vials with B-standard (supplied with the I-CAP), two sample solutions (5% HNO3 + 0.5% HF) and mixed zircon standard (mixed from what is left from last measurement)
9. open ‚Instrument control' and move needle into B-standard
10. in ‚Instrument control' select elements and oxides to measure during tuning (see session excel-sheet or see on the B-standard plastic bottle below the table)
11. start auto-tuning of machine, select high matrix in Wizard
12. open excel-sheet with sessions (D:/Excel files/iCAP Protocoll) and copy the line with the last zircon measurement and fill out values with that shown in the left lower panel in ‚Instrument control'
13. after auto tuning open report and fill values into excel-sheet
14. move needle into sample solution, measured values should be near zero
15. measure zircon mix solution (ZirconJuice)
16. open old measuring file in ‚Qtegra', change name and save it
17. copy and paste sample names, rack Nr is 3 and vial nr is 1 to 90 and 1 to 10 (if 100 samples), main run should be 20
18. dummy and acid blank are the same solution (5% HNO3 + 0.5% HF), dummy is only for cleaning, if acid blank is not clean change position with dummy or change vial/replace solution...
19. if enough ZirconJuice is available from last measurement, measure it before each sample block, main run should be 10
20. in ‚Instrument control' de-select elements and oxides and newly select the following elements and oxides: 91-Zr, 230-Th, 232-Th, 233-U, 235-U, 238-U
21. No mass-bias correction is applied. Each analysis consists of 20 main runs with 14 cycles each. Dwell time is 0.03 s except for 91-Zr (0.01 s) and 235-U (0.05 s).
22. put samples, teflon blanks and Nb-blank in rack 3, make sure that the plastic block is placed below the rack (required because less solution is used)
23. start analysis by pressing start in ‚Qtegra'
24. if needle is going into the teflon blank for the first time adjust the submersion depth
25. check if calibration solution and first sample are running correctly, also check if isotope ratio of spike isotopes is constant for samples (should be around 1)
26. activate the option that after the sequence is finished the I-CAP is going into standby

Export results

1. export average values with standard deviation and sample names
2. export raw data with sample names and measurement date

Rebuild machine

1. if machine is in standby, close water valves
2. changes the washing agent bottle and protect the outlet with parafilm
3. take out the sample and skimmer cone and put it into their storage boxes (possibly clean the skimmer cone; ask Bernhard for help)
4. leave the screw that holds the sample cone on the table (on a clean tissue and covered by a plastic lid)
5. loose the tubes of the peristaltic pump
6. disconnect the gas tube and take out the spray chamber and put it into a plastic bag
7. move the needle out of the washing agent and loose the screw that holds the sample needle
8. pull the tube and needle out of the sampling box and put it into a plastic bag

Calculate results (see ‘Calculate_Ages’ wiki for details)

1. merge exported raw data spreadsheets (exported with Qtegra)

2. copy all columns except for A-D and transpose to new excel-sheet and save as ZrXdateX.xlsx (e.g. Zr160210.xlsx)
3. open matlab and go to He_Age folder
4. Open the script calc_He_age.m and change file name of 'ICAP-file', change values of ‚mainruns', ‚masses' and ‚majorElement' if necessary
5. run script
6. choose 2 as output option

Clean PFA vials for zircon (U-Th)/He:

1. Discard remaining sample and rinse with H_2O
2. Wipe inside with q-tip
3. Soak vials and lids separately in PFA bottles in soap solution overnight
4. Drain soap, rinse 3x in H_2O millipore
5. Soak in 6M HCl on heating plate at 50-120°C for 3 days
6. Drain, rinse 3x in H_2O millipore
7. Soak in 3M HNO_3 on heating plate at 50-120°C for 3 days
8. Drain, rinse 3x in H_2O millipore
9. Soak in H_2O on heating plate at 50-120°C for 1 day
10. Drain, rinse 3x in H_2O millipore
11. Store in H_2O Millipore

Clean PTFE liner and carousel for zircon bombs:

1. Rinse in H_2O
2. Fill in small amount of 6M HCl, place carousel inside liner
3. In digestion bomb heat to 200°C and let cool to vacuum close the liner
4. Open and rinse 3x in H_2O, soak overnight in H_2O
5. Trays are only wiped clean with soap and rinsed with H_2O