

QUARTZ SEPARATION BY SELECTIVE ETCHING WITH HF

Summary

For preparing very pure quartz separates. Most silicate minerals dissolve faster than quartz in dilute HF and can be etched away to leave a very pure quartz residue. Some quartz is lost - usually ~10% of coarse-grained fractions (500-850 μm) and up to 20-30% of fine-grained fractions (250-500 μm). It is difficult to get good yields from this procedure using grainsizes <250 μm .

Some minerals will not dissolve (e.g. garnet, zircon, rutile, ilmenite). Fortunately, except for garnet, these are trace constituents of most rocks. Muscovite is the only other common mineral that causes problems. It dissolves at about the same rate as quartz, so the procedure won't concentrate quartz relative to muscovite.

An initial heavy liquid separation will remove garnet and muscovite (as well as most other mafic silicates and oxide minerals), if present. However, not all rocks need to be processed in heavy liquids before the HF treatment. Small amounts of zircon, ilmenite, etc. in the final sample do not cause problems in the Al-Be extraction chemistry.

Version

This version checked and updated by John Stone, December 2001.

References

This procedure is based on a method published by Kohl and Nishiizumi in 1992. Their paper showed how to produce the high-purity quartz separates needed for ^{26}Al measurements and played a major role in making cosmogenic nuclide analyses of quartz practical and efficient. Please cite:

Kohl C. P. and Nishiizumi K. (1992) Chemical isolation of quartz for measurement of *in-situ*-produced cosmogenic nuclides. *Geochimica et Cosmochimica Acta*, **56**, 3583-3587

if you use this method.

Sample pre-treatment and loading

Pre-clean samples with hot 2% HNO_3 . All carbonates must be removed before reacting the samples with HF. If necessary, separate the "quartz" fraction ($2.63 \text{ g/cc} < r < 2.67 \text{ g/cc}$) in heavy liquid.

Judge the amount of sample, aiming to finish up with 20-40 g of quartz after the full clean-up procedure. If you've done a density separation, use the entire "quartz" fraction. This procedure will remove composite grains and most minerals other than quartz likely to remain in the $2.63 \text{ g/cc} < r < 2.67 \text{ g/cc}$ density fraction.



Label a clean 1 liter polyethylene (PE) bottle twice with the sample name or number.

Transfer the sample to the bottle using a clean plastic powder funnel. Slurry the last grains through with water from a wash bottle.

Fill the bottle to ~ 1" below the neck with "lab distilled" (DW) water.

Rinse the funnel thoroughly before using it for the next sample.

BEFORE PROCEEDING — WARNING: Contact with hydrofluoric acid is extremely dangerous. Burns from small amounts of concentrated HF (48-50%) can be lethal. Read the safety literature. Wear heavy nitrile gloves, apron, sleeve guards and face shield throughout the following procedure. Wear sturdy clothes and shoes when working with HF and around the HF process bath. Know where the calcium gluconate is kept and how to use it to initiate treatment for any contact with HF. Know where the eyewash stands and emergency shower are located. Wipe up any drops (even suspect droplets) with multiple wet paper wipes and soak under running water for several minutes before discarding. Never dispose of HF-contaminated material in the trash. Neutralise waste solutions in the HF waste container.

HF addition - first treatment

In the fume hood, dispense 40 ml of concentrated (48-50%) HF into each sample bottle. The final solution strength will be ~2% HF or ~1.15 M HF/liter.

Gently squeeze each bottle before capping. This gives the contents room to expand when the bottle heats up. Also, loss of vacuum will alert you to the possibility that the bottle has leaked.

Check that the bottle is tightly sealed and holding its slight vacuum. In the fume hood, gently invert it 3-4 times to mix the contents.

Mark the bottle to indicate how many times the sample has been processed

Place it in the sonic bath and process at 69°C for 99 minutes (these are the maximum temperature and time for the Branson ultrasonic baths).

Repeat the processing for 2-3 days. Turn the heat down to 50°C and top up the bath at the end of each day. (Re-set the sonic bath for a final 99 minute run at the end of each day). The sonic action compacts the the grains together and, especially in the initial stages of the reaction, can produce very firm aggregates of clay and fluorides on the floor of the bottle. *Re-suspend the sample to break up these aggregates by inverting the bottle several times, each time you re-start the bath.*



Second treatment

After the first 3-day process, change the HF as follows:

Cool and dry the bottle. Uncap it in the fume hood and discard the contents in the HF waste bin.

Rinse the remaining grains thoroughly with 3 changes of water, decanting off the rinse water while any clay or fine, milky fluoride precipitate is still suspended, but after “fine sand”-sized grains have settled. Don't worry about losing some of the very fine grains, unless the sample is unusually small.

Top up the bottle with DW water to ~ 1" below the neck.

Add 20-40 ml of HF (depending on how clean the sample is after the first treatment) and repeat the ultrasonic processing for a second 2-3 day period.

Sample recovery

After the second 3-day treatment, inspect the sample for purity. Pure quartz samples have a uniform appearance and do not cake on the floor of the bottle. Impure samples usually appear speckled and may contain a cloudy fluoride precipitate.

If the quartz appears pure, recover the sample:

Cool and dry the bottle. Uncap it in the fume hood and discard the contents in the HF waste bin.

Rinse with at least 3 changes of water, as above. Try to rinse away any trace of milky fluoride. The rinse water must be clear (and absolutely free of residual HF) before transferring the sample to a glass beaker.

Label a small glass beaker (a tall-form 200 ml beaker is best).

Now swirl the sample in a little water and tip it into the beaker. It may take 2-3 rinses to transfer all the grains.

Rinse 4-5 times with lab “DW” water, then 2-3 times with high purity DI water. Be sure to mix and re-suspend all the grains during rinsing. Any fluoride or acid left among the sample grains will cause them to cake up when dried.

Dry overnight in the oven.

Cool the sample and transfer it to a labeled ziplock bag. Label this fraction “final quartz” to indicate that it has been purified in HF.

Place the sample in the holding bin to await an ICP check for Al, Fe and Ti.

