

# Can the Picotrace system dissolve zircons?

## Zircon experiment 1

For this experiment I used a granodiorite gneiss (WD-507D), a sill of the Hardwick pluton in west-central Massachusetts, U.S.A. This rock has nearly 500 ppm Zr, and zircons up to 125  $\mu\text{m}$  long and 50  $\mu\text{m}$  across. Its age is latest Devonian, though it may have been substantially heated later in the Paleozoic. The sample was crushed using a Rocklabs tungsten carbide ring mill, and 200 mg of sample was added to each of 16 vessels.

1. To half of the vessels, 3 ml of  $\text{HNO}_3$  (70%) and 3 ml of  $\text{HF}$  (50%) were added, and the samples run with a program that heated them to 175°C over 2 hours, and were held at this temperature for 24 hours. The samples were then evaporated to dryness. The purpose of this pretreatment step was to see if removing most silica first would hasten later zircon dissolution. It did not.
2. To all 16 vessels 6 ml of  $\text{HF}$  (50%) was added, and the samples heated according to the same program as in Step 1.
3. Two vessels were removed and set aside, and the rest put through another heating cycle. This was repeated for the next 7 cycles, so in the end there was a set of pre-treated and not pre-treated samples spanning  $\text{HF}$ -only reaction times of 1 through 8 days.
4. All samples were evaporated to dryness.
5. To all samples was added 15 ml of water and 4 ml of  $\text{HNO}_3$  (70%) to put soluble solids into solution
6. Samples were re-heated for 1 day.
7. Each resulting sample was decanted into a conical-bottom test tube, and gently rinsed several times to remove acid.
8. Residue was transferred to a watch glass and inspected under a microscope.
9. Bottom line: The pre-treatment step (1) had no significant effect in the amount of residual zircon after one day. No zircons were found in samples heated longer than three days. This procedure therefore works for this sample and these zircons.

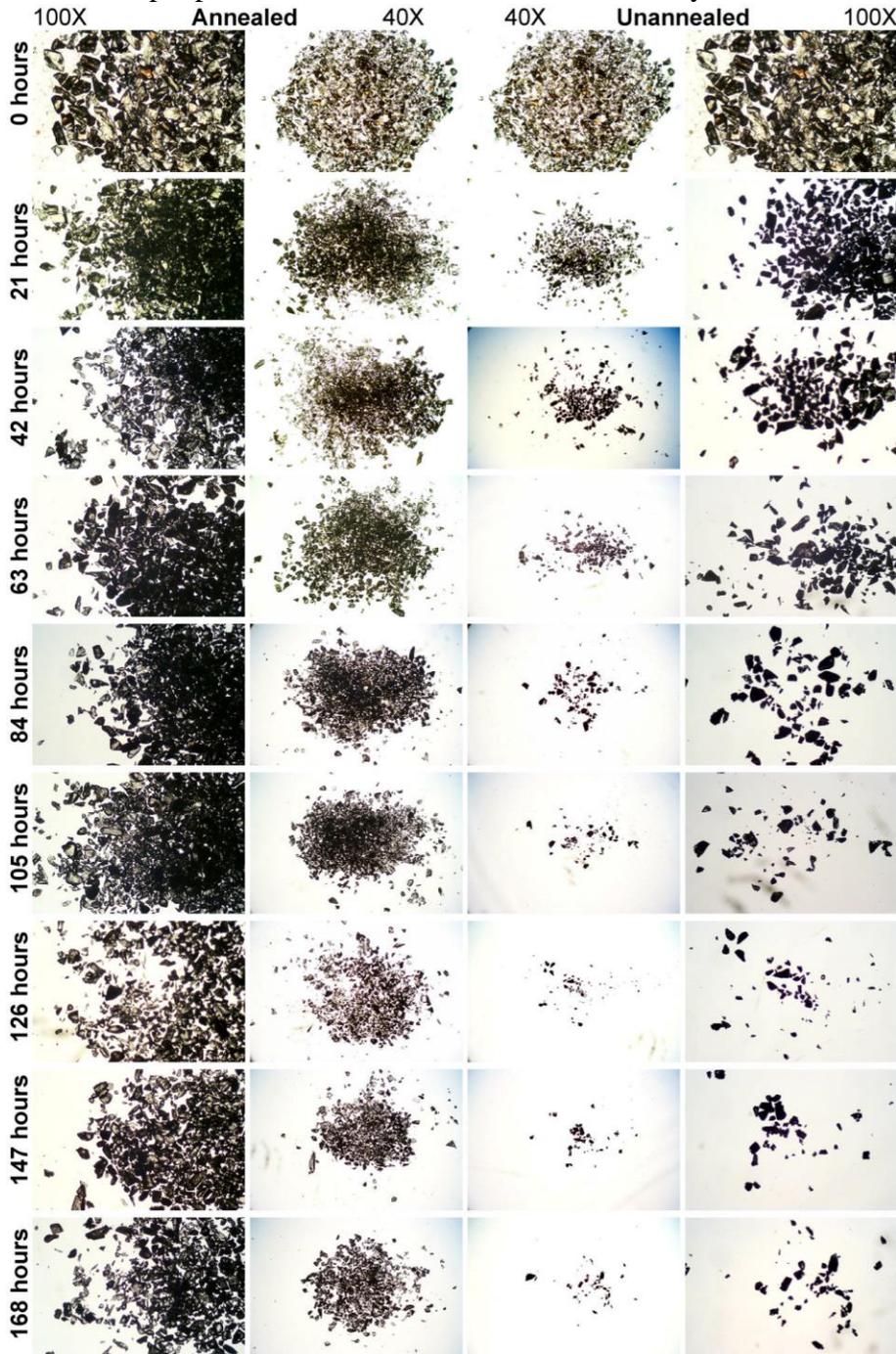
## Zircon experiment 2

In this experiment I tried dissolving pure zircon.

1. I took two big zircon crystals 0.8 cm across (locality unknown, but from the same place). One was annealed at 1000°C for 3.5 hours to remove radiation damage. The annealed zircon therefore mimics young zircons. These were hand-crushed in a Plattner mortar and sieved, and the 70-250  $\mu\text{m}$  fraction retained used for the experiment.
2. 10 mg of the zircons were weighed into sample vessels, 8 for the annealed zircon and 8 for the unannealed.
3. 6 ml of  $\text{HF}$  (50%) was added to each sample, and the vessels heated to 175°C over 2 hours and held at that temperature for 21 hours. Thus, there was no pretreatment step.
4. After one heating cycle, one annealed and one unannealed sample were removed. Most of the  $\text{HF}$  was removed from these by pipette, and the remaining  $\text{HF}$  serially diluted by adding DI water and pipetting away most of the mixture. 15 ml of water and 4 ml of

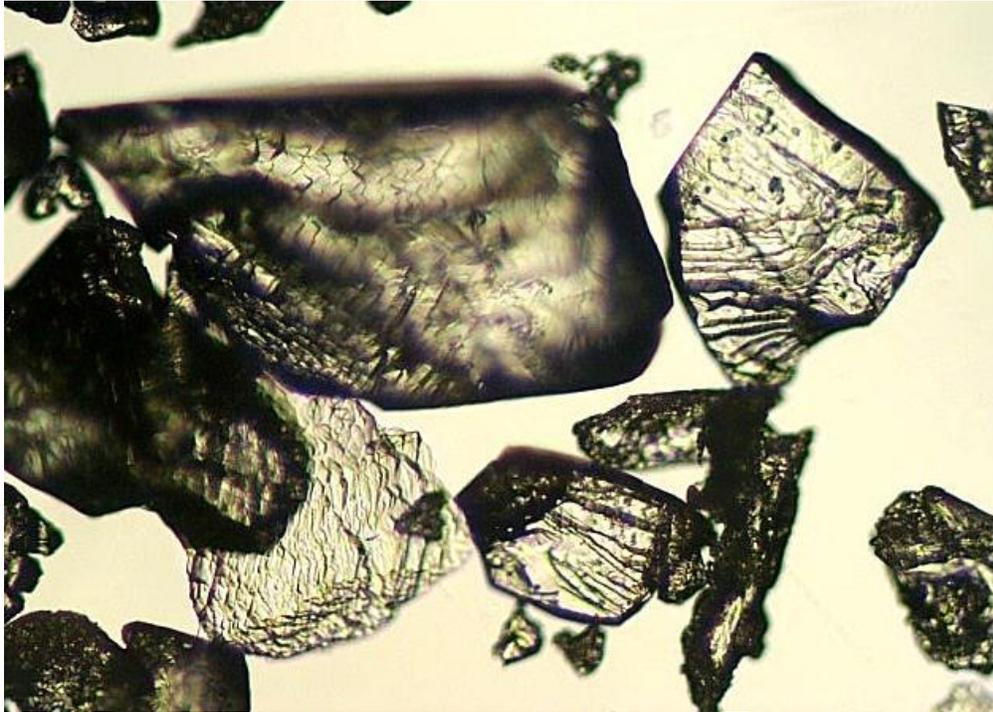
HNO<sub>3</sub> (70%) was added to these samples and then they were put back in the heating block for a heating cycle with the remainder of the samples which still had HF. This step was to remove any tiny amount of insoluble fluorides that might have precipitated from minor components in the crushed zircon samples.

- The next day, the HNO<sub>3</sub> solutions from the previous cycle were decanted and washed into conical-bottom test tubes and diluted, and later examined under a microscope and photographed. Two more HF-bearing samples were removed and subjected to the treatment described in Steps 4 and 5. The end result is that annealed and unannealed sample pairs were heated for between 1 and 8 cycles.

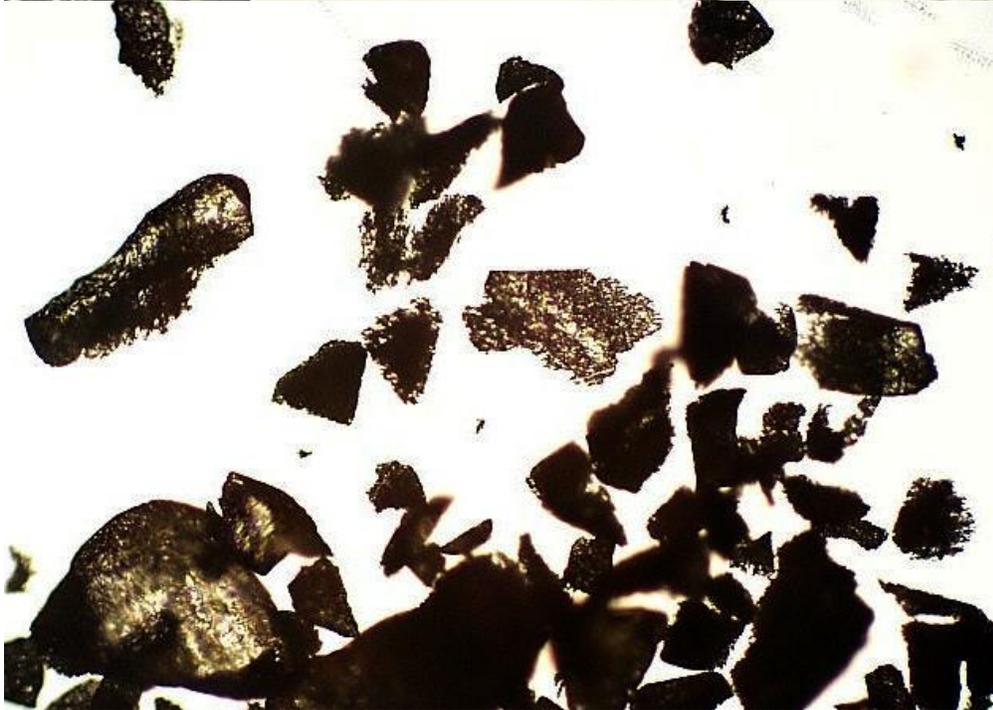


The figure shows the results. This experiment was a stringent test of zircon dissolution because the zircon sieve fraction used was relatively large, probably larger than most zircons in igneous rocks after ring mill crushing, and because half of the zircon samples had their radiation damage annealed. The top row in the image shows 10 mg of raw zircon prior to any treatment with HF. Subsequent rows show the zircon quantity remaining after each of the eight dissolution runs. For the unannealed zircon, roughly 5% remained after 63 hours and perhaps 1 or 2% after 168 hours. For the annealed zircon dissolution was considerably slower, with perhaps 50% of the zircon left after 63 hours and perhaps 20% left after 168 hours. The annealed zircon

remaining after 168 hours is somewhat more than that left of the annealed zircon after 21 hours. Clearly, pure HF is not capable of decomposing all of the, large radiation damaged zircons even after 168 hours (7 days), though perhaps 98%+ is enough for most applications. Recall that experiment 1, above, had no discernable zircon remaining after three days, though those zircons were from a very different source and were smaller.



This is a photo of the annealed zircons after 63 hours, 200X. The surfaces are covered by a series of steps, suggesting that dissolution is fastest along step edges. Small rectangular pits are also common, though only a few are visible here, on the grain to the upper right.

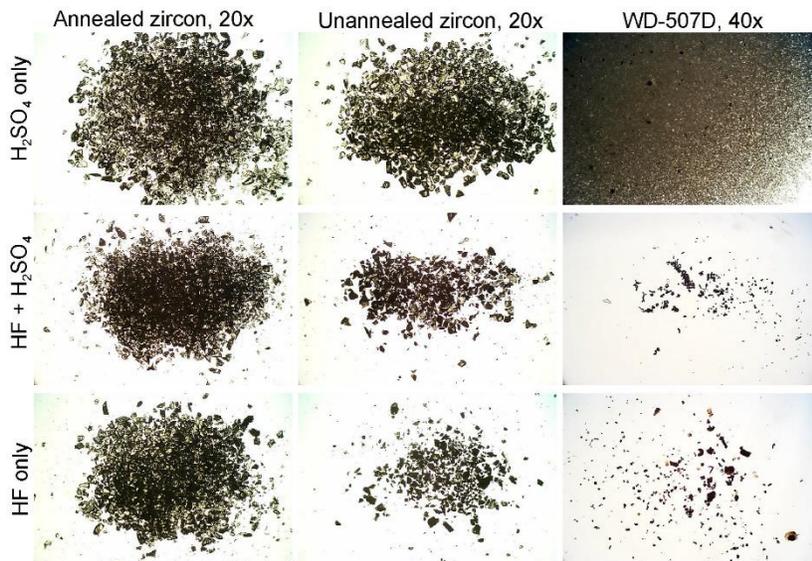


This is a photo of the unannealed zircon after 63 hours, 200x. The zircon surfaces are spongy, with dissolution preferentially following radiation damage tracks. Note that the grain size is generally smaller than in the photo above.

### Zircon Experiment 3

The Picotrace literature has the following procedure for dissolving zircons:

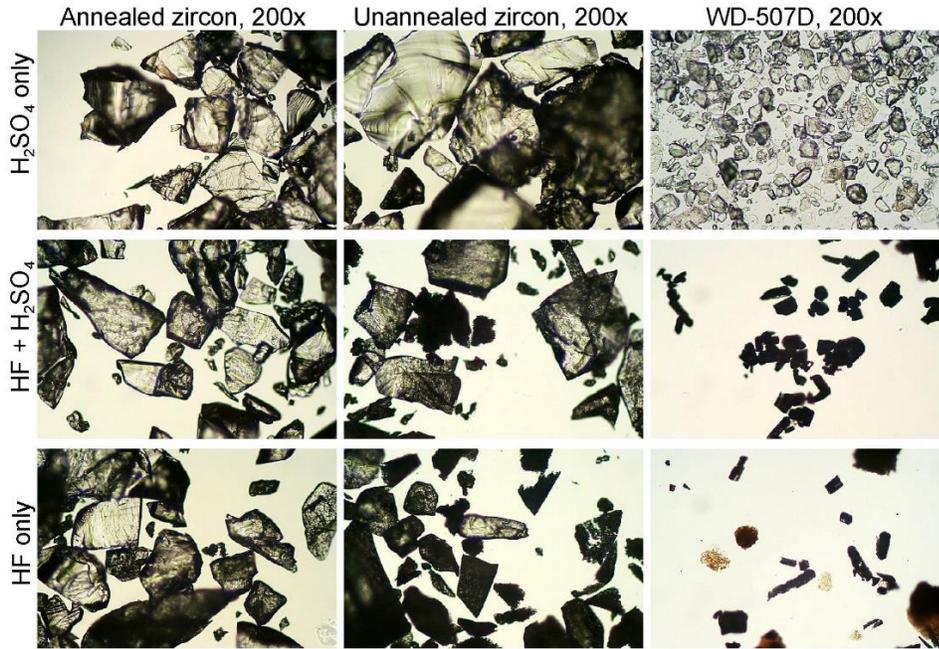
	Picotrace-suggested dissolution procedure	The procedure I followed
1)	Weigh 100-200 mg of rock powder into sample digestion vessels.	Weigh 200 mg of WD-507D rock powder (experiment 1, above) into 3 vessels. Weigh 10 mg of annealed zircon (experiment 2, above) into 3 vessels. Weigh 10 mg of unannealed zircon (experiment 2, above) into 3 vessels.
2)	Add to vessels 3 ml of HF and 3 ml of H <sub>2</sub> SO <sub>4</sub> .	To 1 vessel of each sample type, add 3 ml of HF and 3 ml of H <sub>2</sub> SO <sub>4</sub> . To 1 vessel of each sample type, add 6 ml of HF. To 1 vessel of each sample type, add 3 ml of H <sub>2</sub> SO <sub>4</sub> .
3)	Heat to 180°C over 3 hours and maintain for 15 hours.	Heat to 175°C over 2 hours and maintain for 24 hours. Note, at that time we could not get the vessels to 180°C, <a href="#">but now we can</a> .
4)	Evaporate the acid at 180°C for 100 hours.	Evaporate the acid at 185°C for 96 hours. Note that a higher temperature was attained with the evaporation lid, presumably because it insulated the digestion block better than the high-pressure lids. Note that about 2 ml of H <sub>2</sub> SO <sub>4</sub> remained in each of the 6 vessels that started with any, so evaporation was continued for another week! It may be that our air flow during evaporation was too low, because of collapsed aspiration bottles.
5)	Add 2 ml of HNO <sub>3</sub> and 2 ml of 6 N HCl.	Add 4 ml of HNO <sub>3</sub> and 15 ml of water.
6)	None	Heat at 155°C for 21 hours to facilitate dissolution. Minor fluorides remained in the HF-only, WD-507D vessel. This indicated that a more concentrated acid solution was needed, or a second evaporation step with HNO <sub>3</sub> to drive off more of the initial fluorides. This is part of our <a href="#">standard dissolution procedure</a> .



The residue from dissolution was transferred to 50 ml conical-bottom test tubes, washed with DI water, concentrated in a watch glass, and photographed in the same way as in Experiment 2, above.

This photo shows results for the three sample types (annealed and unannealed zircon, WD-507D granodiorite gneiss), and three sets of acids: H<sub>2</sub>SO<sub>4</sub> only, HF + H<sub>2</sub>SO<sub>4</sub> as recommended by Picotrace,

and HF only. In the first row it is clear that zircon is unimpressed with  $H_2SO_4$ , as are most other silicates in WD-507D. In the second row, representing dissolution conditions close to that recommended by Picotrace, it is clear that the dissolution of zircon is incomplete in all three samples. In the third row, with HF only, dissolution is also incomplete, as was found in Experiment 1 for sample WD-507D, and in Experiment 2 for annealed and unannealed zircon after heating for only 21 hours. The  $H_2SO_4$ -only zircon samples here look much like the zero-hour samples in Experiment 2, and that the HF-bearing zircon samples look very much like the 21 hour samples in Experiment 2. This suggests that the  $H_2SO_4$  is doing nothing special as far as zircons are concerned.



Here are close-ups of the samples above, arranged in the same order. In the first row with  $H_2SO_4$  only, all zircons appear fresh and unaffected, as do quartz, feldspar, and zircon in WD-507D. In WD-507D, Fe-Ti oxides have been decomposed, as has all biotite. In the second, mixed acid row, etching is evident in all samples, though etching relatively

minor in the annealed zircon. In the third, HF-only row, etching is somewhat stronger.

Although there were some minor differences between the procedure I followed here and that recommended by Picotrace, I doubt they are significant. The HF- $H_2SO_4$  procedure does not seem capable of dissolving zircon in these samples.  $H_2SO_4$  seems to do nothing but dilute the HF. My recommendation is to follow [our procedure](#).

The End.