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A safe procedure for HF etching as part of sample preparation for luminescence dating

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Abstract

This paper presents a protocol for safe quartz etching with hydrofluoric (HF) acid as part of sample preparation for luminescence dating. Concentrated HF is extremely hazardous and can cause severe burns and poisoning, even leading to death. Generally, in order to avoid exposure to light and bleaching, HF etching is performed in a dark laboratory under weak orange-red light in wide-open beakers. Handling HF in open beakers in the dark could result in unfortunate accidents due to unintentional spillage. The presented protocol avoids these two main safety issues – working with open beakers and under poor lighting. The samples are etched inside black opaque bottles with narrow openings so that the procedure can be safely performed in comfortable light levels. To validate the harmlessness of the laboratory environmental light, bleaching experiments of quartz were conducted under the same conditions as the protocol. These showed that no bleaching occurred during this procedure.

Keywords: Hydrofluoric acid, Quartz-etching

1. Introduction

Extraction of quartz and alkali-feldspar (KF) grains for luminescence dating includes etching with hydrofluoric (HF) acid (Aitken, 1985; Wintle, 1997), which is highly corrosive. Different laboratories have varying practices, but generally, quartz grains are etched with concentrated HF (40 – 48 %) for at least 40 minutes. This step is essential for dissolving feldspars, removing clay or iron oxide coating on the grains, and etching the outer rim of the quartz grains affected by alpha particles during burial. Regarding KF etching, the procedure is less uniform across laboratories. As feldspar is affected much faster by the HF, the grains are usually etched with diluted acid (10 %) for various durations (0 – 40 min). Porat et al. (2015) investigated the KF grain size reduction by different HF treatments and suggested etching the feldspars with 10 % HF for 10 min.

HF acid is extremely hazardous as it can cause severe burns and poisoning (Bertolini, 1992; Wang et al., 2014), even leading to death (Muriale et al., 1996). Therefore, it should be handled with extra caution, and any work with it should be carried out in designated fume hoods. For safety, one usually wears additional protective clothing such as a lab coat, closed shoes, protective goggles, suitable gloves, a rubber apron, and rubber sleeves.

Generally, in order to avoid exposure to light and bleaching, the HF etching procedure is performed in a dark laboratory under weak orange-red light in wide open beakers using access HF acid. Even when taking all precautions, handling HF in open beakers under insufficient light could result in unfortunate accidents due to unintentional spillage.

The luminescence laboratory at the Geological Survey of Israel (GSI) developed a protocol for HF etching that avoids the two main safety issues – open beakers and poor lighting. The protocol was tested on samples that had also been prepared in other laboratories using more conventional protocols, such as coastal sediment from the Skagen peninsula, Denmark, and no difference was found in the measured D_e values (Murray et al., 2015). Here, we describe the safe procedure for HF etching as part of sample preparation for luminescence dating.

Figure 1. Setting of the HF etching procedure within a chemical fume hood. a) The HF is transferred from the HF bottle to the sample bottles through the peristaltic pump. The cup connected to the pump tube (sample closest to the pump) is moved from one sample to the next. b) The bottle cap that is moved from sample to sample has two holes, one with the exact diameter of the tube, where it is placed, and a smaller one to release air. c) After 40 minutes of soaking, the spent acid is carefully poured into a waste bottle. Note that the sample will settle in the shoulder of the bottle.

2. Procedure description

The HF etching protocol uses 250 mL black, light-tight polyethylene bottles with caps and a narrow opening that prevents any light from reaching the bottom of the bottle (Fig. 1). About 3 g from each sample is weighed into a bottle in the dark, and the cap is replaced. From this step, the procedure is continued with comfortable light levels within a chemical fume hood. If there are no windows introducing daylight into the preparation laboratory or white light lamps, this procedure can be carried out at any chemistry laboratory. A fixed amount of HF (5 mL per 1 g quartz) is pumped into the bottles one after the other using a calibrated peristaltic pump and a timer. Each sample is soaked for 40 minutes in the HF. During this time, the bottles are repeatedly shaken every few minutes. After 40 minutes, the spent acid is poured out into a designated waste disposal container (Fig. 1), and the bottle is filled with water for a first rinse. After about a minute, this first rinse is carefully poured out, and water is added for a second rinse, after which the bottle is closed and ready to be returned to the dark lab. There, each sample is transferred to a corresponding beaker for three additional rinsing steps. Then, the samples are placed in 16 % HCl overnight to dissolve fluorides. The next day, the samples are thoroughly rinsed and dried, ready for measurements. For safety reasons and convenience, this protocol is carried out by two people, although one can easily do it alone.

Peristaltic pumps are used in geochemistry laboratories to transfer solutes into analytical instruments. Their advantage is that they are quiet, can be adjusted to pumping exact volumes over a given time, and when turned off, the pipe with the acid does not drip, so that the HF does not drip in the few seconds, it takes to transfer the pipe from bottle to bottle. Before starting, one should calibrate the volume of the liquid pumped over one minute (no need to use HF for that; water is just as good). Hypothetically, the pump can work faster and pump the required HF volume over less time so that more samples can be etched in a single batch. Depending on the available pumping rate and amount of feldspar contamination, each laboratory can work out their batch so

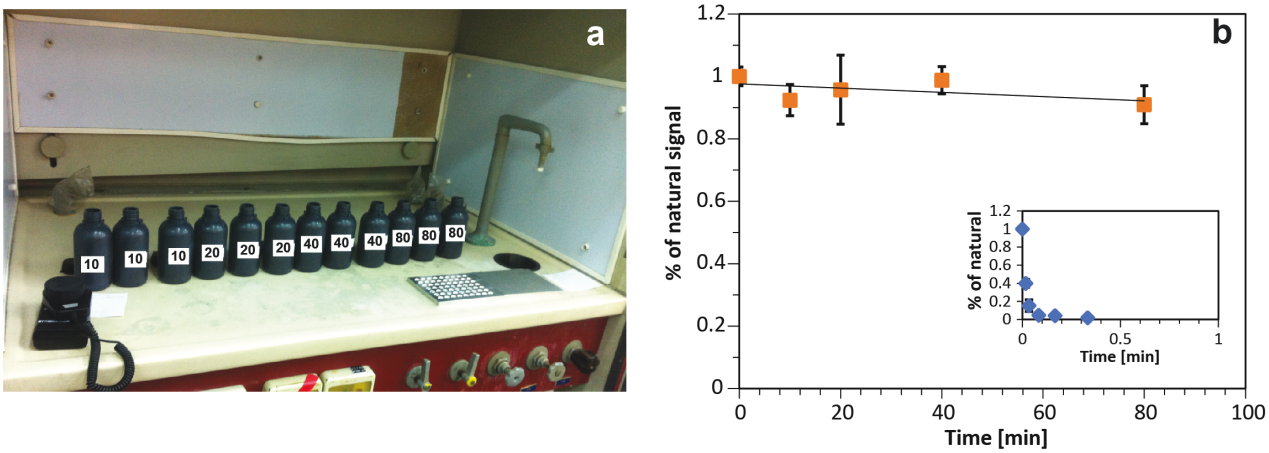

Figure 2. Quartz bleaching experiment inside the black bottles used for HF etching. a) The experiment setup within the fume hood. One disc is settled in each bottle. The numbers on the bottles are the bleaching durations in minutes. b) The experiment results. The inset–bleaching experiment results in full sunlight.

that it would finish well under 40 minutes (or the laboratory's standard etching time).

The amount of quartz etched from each sample is usually 3 g – if available – or less. Three grams were found to be sufficient even if half the amount was lost by dissolution and some spillage during rinsing. Even if only 1 g remains, one can make more than 100 x 9 mm aliquots or 1000 x 2 mm aliquots. Smaller quantities require more careful handling, but even 200 mg of final weight is sufficient for ordinary samples. Smaller amounts of quartz mean less HF used, which is beneficial on all accounts.

Following the recommendations of Bell & Zimmerman (1978) and Aitken (1985), it is postulated to etch the outer 10 mm of the quartz grains to neglect the alpha radiation from the dose rate evaluation. For etching quartz, about 5 mL of HF for each gram of sample is sufficient. Adding more acid does not remove more than the required 10 µm (Porat et al., 2015). However, if large amounts of feldspars are present (e.g. when samples are treated to only a single density separation of 2.62 g cm^{-3}), the volume of HF should be doubled or even tripled to allow the complete dissolution of feldspars.

Before the etching procedure, it is essential to ensure that all the carbonates in the sample have been dissolved in advance by HCl. Any remaining $CaCO_3$ will strongly react with the HF and form hard-to-dissolve calcium fluorides. Porat et al. (2015) showed that even after complete carbonate dissolution, some fluorides are still formed during the HF etching process. The source of the Ca is probably from plagioclase in the sample. Nevertheless, these dissolve later in the following HCl treatment (Porat et al., 2015).

Here is a working example from the GSI for a 40 minutes etching (procedure video is available at `https://youtu.be/lZbMpKDgf-s`): There are 18 samples in a batch. Three grams of quartz are weighed from each sample. Most samples contain little feldspars, so 15 ml of HF (5 mL x 3 g) is sufficient. The pump is set for a flow of 10 mL per minute, so the pumping time is 1.5 min. With 15 – 20 seconds added for moving from sample to sample, it takes roughly 1.75 min per sample. This works out fine as the filling time for the 18 samples will be 1.75 min x 18, i.e. 32 minutes. Thus, pumping HF to the last sample ends about 8 minutes before the first sample needs to be rinsed, leaving time for the unexpected.

HF etching affects grain's morphology differently, depending on their content, structure, and sedimentary maturity (Bell & Zimmerman, 1978; Porat et al., 2015). Duval et al. (2018) recommended that each laboratory evaluate the outer rind thickness etched by their procedure. For the presented procedure, it was reported on removal of 10 – 50 µm from the quartz rims depending on the sedimentological maturity and mineral purity (Porat et al., 2015). For quartz grains of mature sedimentary origin, 10 µm were etched as desired. For grains from immature sources, the grain size was reduced by up to 50 µm, primarily due to breakage along etched plains. Therefore, after the HF etching, for immature sediments, it is recommended to sieve at 20 µm below the original grain size to get rid of the broken grains.

3. Bleaching experiments

As the procedure is performed under regular laboratory fluorescent light, it was essential to ensure that the luminescence signal of the samples does not undergo any bleaching. In order to do so, a bleaching experiment was conducted. Five mm aliquots of purified quartz (sample FGA-26 from Faershtein et al. 2016) were placed in empty, open 250 mL black bottles, used for the HF etching procedure, for different periods of time up to 80 min, with the fluorescent lights turned on (Fig. 2a). Three aliquots were used for each bleaching duration (each aliquot was placed in a separate bottle). The bottles were placed 25 cm from the fume hood opening. The average light intensity next to the bot-

tles was measured at 170 lux. For comparison, a bleaching experiment was also conducted for the quartz grains in full sunlight (light intensity was measured at 57000 lux).

The experiment indicates that after 80 min inside open black bottles, the OSL signal is reduced by up to 10 % of the original signal (Fig. 2b). Some of the aliquots are not bleached at all. One of the aliquots that was bleached for 10 min showed a bleaching of 13 %, increasing the average bleaching for this duration. It is possible that the disc was accidentally exposed to direct fluorescent light during the experiment's setup. Excluding this disc, after 10 min of bleaching within the black bottles, the signal was bleached by 5 %. In contrast, in full daylight, the OSL signal of the quartz grains is reduced to less than 5 % after 5 s. It is important to note that while in the bleaching experiment, the black bottles were left open for the entire experiment time, during the HF etching procedure, the cap is removed only for a few seconds. Also, during the experiment, all the fluorescent lights in the laboratory were turned on, while during the procedure, we turn off the lights near the fume hood. Therefore, there is no risk of bleaching during this protocol.

4. Summary

We described a protocol that avoids the most risky factors of using HF in luminescence dating: working in the dark and pouring HF into open beakers. Any lab that had a beaker accidentally turned over would appreciate it. It is also light-safe and avoids any access exposure of the samples to laboratory light. This protocol was devised over 22 years ago and has since been used 10 – 15 times yearly. Not a single accident with HF body exposure happened during that time. This protocol is also economical regarding HF; only 15 mL are used per sample. We deem this protocol as very safe and encourage other laboratories to adopt it or a variation of it.

Appendix: HF etching protocol

Equipment list:

1. Samples (18 in the case of the GSI)
2. Labeled black, opaque polyethylene bottles with caps, one for each sample; 1 cap has two holes for the tube and air.
3. Suction tube with stopping restrains, about 60 cm long
4. Peristaltic pump, calibrated (calibrated pumping rate at the GSI is 10 mL per minute)
5. Concentrated HF acid (40%) bottle with a narrow opening (Fig. 1a)
6. Any plastic bottle (250-500 mL) with a tight screw cap to collect the spent HF, to be later disposed with other chemical waste.
7. Timer
8. Watch with minutes

Procedure

In the dark lab:

- Weigh about 3 g sample into a bottle and close with the cap.
- If there is less than 3 g of quartz, mark the weight on the label.
- Repeat for all samples.

In a lit lab in a fume hood (procedure video is available at `https://youtu.be/lZbMpKDgf-s`):

- Put on safety gear.
- Turn off fluorescent lights near the fume hood but leave other lights on for comfortable vision; turn on ventilation in the fume hood.
- Set up the peristaltic pump. Put one end of the tube into the HF bottle and the other into the black sample bottle lid with the holes.
- Turn on the pump and turn on the timer, wait the designated time (marked by the timer), and turn the pump off (for the first sample, start the timer only when the acid reaches the sample bottle).
- The pierced lid with the tube will now be passed to the following sample, while at the same time, a normal lid will be placed on the sample that has just received HF. Partially close the lid on the first sample to allow for any gasses to be emitted and, at the same time, prevent unnecessary exposure to light. Exchange lids as quickly as possible.
- Repeat for all samples. From time to time, twirl the waiting bottles. In the last sample, take the tube out of the HF bottle after a minute and let the tube empty into the black bottle.

After 40 minutes of introducing HF to the first sample:

- Open the first sample and carefully drain most of the spent HF into the waste bottle. The grains will collect in the bottle's shoulder. Add 200 mL water, close, and set aside. After the following sample is drained and filled with water, return to the first sample, slowly pour most of the water into the sink while the water is running, and refill with ~200 mL water. Close the bottle tightly and place it away. Your first sample is done.
- Continue with the next bottle. Note that one rinse takes place right after draining the HF, the second a few minutes later, after the following sample has been drained. That leaves time for the grains to settle.
- If there is a very little sample (less than 0.5 g), leave it in HF for only 20 minutes so that not all is dissolved, and be extra slow and careful when pouring out and rinsing.
- Now the samples are ready to be returned to the dark lab for additional rinsing and following quartz extraction steps.

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Reviewers

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