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www.ancienttl.org · ISSN: 2693-0935

Duval, M., Guilarte, V., Campaña, I., Arnold, L., Miguens, L., Iglesias, J. and González-Sierra, S., 2018. *Quantifying hydrofluoric acid etching of quartz and feldspar coarse grains based on weight loss estimates: implication for ESR and luminescence dating studies.* Ancient TL 36(1): 1-14.
https://doi.org/10.26034/la.atl.2018.522

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Quantifying hydrofluoric acid etching of quartz and feldspar coarse grains based on weight loss estimates: implication for ESR and luminescence dating studies

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Received: April 19, 2018; in final form: April 20, 2018

Abstract

A series of hydrofluoric (HF) acid etching experiments were performed on several 50 to 300 μm (nominal sieve opening) quartz and feldspar samples, and average etching thicknesses were subsequently determined from weight loss estimates, following the approach of Bell & Zimmerman (1978). Our results are consistent with previous studies and confirm that both HF experimental conditions (etching time, HF concentration, agitation) and the nature/origin of the minerals have a significant effect on etching rate and magnitude. For the samples considered in this study, the outer 10 μm of quartz (i.e., the usual etching target in most ESR and luminescence dating studies) was removed with 40% HF after 40 min of etching, in fair agreement with previous studies. Similar etching results were achieved in just over 20 min when the quartz samples were constantly agitated during 40% HF treatment. For K-feldspars, 10% HF etching for between 10 and 40 min was required to remove the same thickness, although some variability in etching efficiency was evident between different samples and experimental conditions. For a given experimental setup, the overall variability in etching thickness among quartz samples was found to be of at least 20% after 40–60 min with 40% HF, and can be as high as ∼35%. A set of 14 K-feldspars from a single site revealed an inherent variability of 14% in etching thickness. As a first order approximation, these data may provide useful insights into the expected variability among samples of different origin and from a given area, respectively. However, we recommend that each laboratory evaluates etching thickness losses for their specific HF experimental setup. Additionally, our results show that the 10 μm etching usually considered in ESR and luminescence dating studies may reduce the alpha contribution of the total dose rate to <5%. Although relatively small, this contribution is nevertheless non-negligible. Based on these results, it may be worth considering an additional alpha dose rate term as part of the ESR and luminescence age calculation when etching depths are < 15 μm.

Keywords: hydrofluoric acid (HF); etching; Luminescence dating; ESR dating; Quartz; Feldspar; weight loss

1. Introduction

Quantifying the effects of hydrofluoric acid (HF) etching on quartz and feldspar grains is crucial for both Electron Spin Resonance (ESR) and luminescence dating applications. An estimate of the outer thickness removed from silicate grains by HF etching is needed for accurate evaluation of both the internal and external alpha and beta dose rate components (see Aitken, 1985). However, obtaining reliable etching rates is not straightforward owing to a number of sources of variability and uncertainty, including the experimental conditions employed and the nature of the sample considered.

Several aspects of the experimental procedure can significantly influence the rate and magnitude of the HF etching, particularly the temperature of the reaction, its duration, and the concentration of the acid employed (e.g., Leko & Komarova, 1973; Bell & Zimmerman, 1978; Porat et al., 2015). Moreover, earlier studies have shown that, even for a given experimental procedure, etching rate may vary by a factor of > 2 for different quartz samples (Bell & Zimmerman, 1978). In other words, compositionally similar minerals can respond differently to HF treatment, depending on their origin, structure, weathering history or sub-composition. For example, Porat et al. (2015) showed that the mineralogical maturity of a sediment sample has a direct impact on HF etching magnitude.

The most widely used approach to evaluate grain thickness removal during HF etching at a multi-grain level involves weight losses determination: the sample is weighed before and after HF etching in order to estimate the bulk amount of material lost during the etching process (Bell & Zimmerman, 1978, and references therein). Surprisingly, the number of quantitative studies of HF etching rates for quartz and feldspar grains has remained limited since the pioneering works of Fleming (1969) and Bell & Zimmerman (1978). Aside from the assessments of Hong (1998) and, more recently, Porat et al. (2015), little attention has been paid to this question over the last few decades, and the available numerical data in the literature remains scarce or poorly detailed.

In order to provide additional empirical data on this important question, we have performed a series of HF etching experiments on several quartz and feldspar samples of different grain sizes (nominal sieve opening between 50 to 300 μm), using HF at different concentrations (40% and 10%) and durations (10, 20, 40, 60 min). The surface thickness removed by HF etching was calculated through weight loss estimates in order to obtain comparable results with earlier studies.

2. Material

Four commercial natural sand samples were selected for the first two HF etching experiments: three silica sand samples (MS1, MS2 and MS3) and one feldspar-rich sand (MF5). MS1 is a normalized sand (ref. CEN-UNE-EN 196-1) provided by the Instituto de Ciencias de la Construcción Eduardo Torroja (Madrid, Spain) with an initial grain size < 2 mm and a certified SiO_2 content of $> 98\%$. MS-2 is a white sand with an initial grain size of 180-500 μm derived from the Stampian (Oligocene) Fontainebleau sand formation (France). This fined-grain, well-sorted and high purity quartz sand with a SiO_2 content $> 99.5\%$ (French & Worden, 2013) has recently been considered as an appropriate reference material for luminescence dating studies (Kreutzer et al., 2017). MS-3 is a siliceous sand (ref. A-S70) from the Arija Quarry (Spain) and delivered by Sibelco, with a SiO_2 content of $> 90\%$ and an initial grain size of < 1 mm (technical specifications provided by Sibelco). Finally, MF5 is a potassium feldspar sample from Carrascal del Río Quarry (Segovia, Spain), which has been derived from feldspar-rich sands by flotation techniques. Technical specifications provided by Incusa (ref. FK-D) indicate an initial grain size of < 700 μm, a feldspar concentration of $\sim 93\%$ (including $\sim 70\%$ and 23% of K-feldspars and Na feldspars, respectively) and a quartz concentration of $\sim 7\%$.

Another set of 14 natural sediment samples (DY08-9 to DY08-22) was selected for a third HF experiment in order to evaluate the etching rate variability among feldspar grains from a given area. These samples come from alluvial and aeolian deposits preserved on the upper fluvial terrace of the Lena River near Yakutsk in central Siberia (Russia) (Waters et al., 1997).

3. Methods

Sample preparation, HF experiments and Static Image analyses were all carried out at the *Centro Nacional de Investigación sobre la Evolución Humana* (CENIEH, Burgos, Spain).

3.1. HF experiments #1 and #2

Dry sieving was performed on the raw sediment samples (MS1, MS2, MS3 and MF5) using a column of several 200 mm diameter Retsch test sieves of standard mesh sizes ranging from 2 mm to 50 μm. These sieves were mounted on a Retsch AS 200 sieve shaker and sieving time was fixed to 10 min per sample, stopping at intervals of 45 s before restarting. The sediment was collected for standard nominal sieve opening ranges of 100–150 μm and 150–200 μm, which are the most widely used grain sizes in ESR dating of sediment, but also 50–100, 200–250 and 250–300 μm. In order to eliminate possible contamination by other minerals, the sieved fractions were subsequently processed using standard ESR sample preparation techniques: HCl (36%) was used to dissolve carbonates and H_2O_2 (30%) to remove organic matter. Several steps of density separation were carried out using sodium polytungstate (SPT) at d= 2.72, d=2.62 and d=2.58 g/cm^3 (Wintle, 1997) in order to make sure that samples MS-1, MS-2 and MS-3 were only composed of quartz grains and that sample MF-5 only contained potassium feldspars.

Each sample was then divided into several homogenous

Figure 1. Pictures illustrating Experiments #1 (left) and #2 (right).

subsamples (aliquots) by using a Quantachrome Rotary Micro Riffler MRR-11. One aliquot of each sample was kept natural (unetched) and used as a reference, while the others were used for the HF etching experiments. The relative variability in weight among the aliquots of a given sample prior to HF etching was $< 4\%$. Depending on the amount of material available, the initial weight of the subsamples was between 1.5 and 6.5 g.

Two different experiments were performed. For Experiment #1, aliquots of quartz and feldspars (samples MS1, MS2, MS3 and MF5) were transferred to Teflon beakers and covered with 40% or 10% HF for etching times of 10, 20, 40 and 60 min (Figure 1, left). Each beaker was manually agitated and stirred for a few tens of seconds every 5–10 min. For Experiment #2, aliquots of quartz (samples MS1 and MS3) were only treated with 40% HF, and the beakers were placed on a laboratory shaker that agitated the samples along a horizontal plane (Figure 1, right) to ensure more efficient sample mixing and more homogenous etching among grains. An overview of these experimental conditions is provided in Table 1.

HF was systematically added in excess of the selected SiO_2 mass for each sample (between 20 and 60 ml, depending on the aliquot mass considered). Once the required etching duration was reached, the sediment was abundantly rinsed with water (5 times $\sim$200 ml). HCl (30%) was then added in order to remove any remaining soluble fluorides and the sediment was rinsed again, dried overnight at 40 °C and finally weighed. Each set of experiments was carried out within a week at controlled room temperature (25 °C).

3.2. HF experiment #3

14 sediment samples were prepared under subdued red light in the CENIEH Luminescence Dating Laboratory. Coarse-grain K-feldspar fractions were extracted using chemical digestion (30% HCl and H_2O_2 treatment), wet sieving and heavy liquid density separation with 2.53 g/cm^3 and 2.58 g/cm^3 SPT solutions. K-feldspar extracts were transferred to Teflon beakers and etched in 10% HF for 10 minutes following the recommendations of Porat et al. (2015) and treatments adopted in several recent post-IR IRSL K-feldspar dating studies (e.g., Arnold et al., 2014; Demuro et al., 2014). Beakers underwent manual agitation and stirring three times during the etching period (Table 1). The etched K-feldspar fractions were then treated with 30% HCl for 45 minutes to eliminate any acid-soluble fluoride precipitates. The dry weight of each sample was recorded before and after the HF etching procedure, following the same steps outlined in HF experiments #1–2.

To assess the efficiency of our density separation procedures, we measured the bulk K content of two prepared feldspar samples (DY08-21 and DY08-12) using a Risø GM-25-5 beta counter (Bøtter-Jensen & Mejdahl, 1988) at the University of Adelaide's Prescott Environmental Luminescence Laboratory (Australia). For each sample we measured three 100 mg aliquots of prepared material, along with a background standard (MgO) and an aliquot of KCl (known K content = 52.4%; grain size 212–250 μm), following the approach of Bøtter-Jensen & Mejdahl (1985). The bulk K contents of samples DY08-21 and DY08-12 were 12.5 $\pm$ 0.2% and 10.4 $\pm$ 0.2%, respectively, supporting the general purity of the K-feldspar extracts used in Experiment #3.

3.3. Weight loss estimates and associated uncertainty

All of the samples considered in the three experiments were weighed before and after HF etching. A potential source of uncertainty on the weight loss estimates relates to inadvertent grain removal during the washing stages, i.e. when the material is successively rinsed several times with water in order to remove any traces of HF. This potential complication has been assessed in Experiments #1–2 by carrying out an additional control experiment with unetched samples under identical conditions, with the exception that water rather than HF was used during the etching stages. Each blank subsample was washed 10 times to replicate the 5 rinses received following HF treatment and the 5 rinses

Experiment	Samples_Grain size (μm)	HF dilution	Duration of the etching (min)	Comment
#1	MS1_100–150, MS1_150–200, MS2_100–150, MS2_150–200, MS3_100–150, MS3_150–200, MF5_100–150, MF5_150–200	40% and 10%	0, 10, 20, 40 and 60	Manual agitation and stirring every 5–10 min.
#2	MS1_50–100, MS1_100–150, MS1_150–200, MS3_150–200, MS1_200–250, MS1_250–300, MS1_150–200	40%	0, 10, 20, 40 and 60	Continuous agitation
#3	DY08-9 KF_212–250, DY08-10 KF_212–250, DY08-11 KF_212–250, DY08-12 KF_212–250, DY08-13 KF_212–250, DY08-14 KF_212–250, DY08-15 KF_212–250, DY08-16 KF_212–250, DY08-17 KF_212–250, DY08-18 KF_212–250, DY08-19 KF_212–250, DY08-20 KF_212–250, DY08-21 KF_212–250, DY08-22 KF_212–250	10%	10	Manual agitation and stirring undertaken 3 times during the etching period

Table 1. Overview of the three HF etching experiments performed in the present study.

received after HCl treatment in Experiments #1–2. Subsamples were weighed before and after the rinsing process. These control tests were performed with several subsamples of 50–100, 100–150 μm and 150–200 μm fractions of samples MS1, MS2, MS3 and MF-5. As part of Experiment #3, an additional control sample (DY08-7) from the same fluvial terrace site was included to monitor any potential spurious weight losses related to agitation, stirring and rinsing of beakers. Again, this control sample was subjected to exactly the same experimental procedures as the other samples except that water was used instead of 10% HF during the etching stage. The results of these control tests are summarised in Table 2.

Weight losses related to pouring and washing procedures varied within a narrow range (from -2.0 to -3.1%) for 100–200 μm grains in Experiments #1–2 and amounted to -2.7% on average. In contrast, weight losses associated with rinsing were significantly higher for smaller grains, with values ranging from -9.3% for quartz samples to -25.0% on average for feldspar grains. This difference might be due to insufficient waiting times prior to the decantation of the smallest (50–100 μm) grains during the blank experiments. However, despite this uncertainty, one can observe from Figure 2E that all the grain size fractions from 50 to 300 μm have produced consistent weight loss trends (within error) for the main etching tests undertaken in Experiment #2. Consequently, it seems likely that the results obtained from the 50–100 μm fraction during the blank experiment may not be fully representative of the true weight loss uncertainty associated with Experiment #1–2 in this specific case.

In Experiment #3, a relative weight loss of 0% was observed for the larger (212–250 μm) K-feldspar grains of control sample DY08-7 (Table 2). This higher recovery rate compared with Experiment #1-2 may partly be linked to (i) the differences in the sample weights involved in the two sets of blank experiments, i.e. 1.50 g for #3 vs. 0.87–6.37 g for

Experiment	Sample	Grain size (μm)	Initial weight (g)	Final weight (g)	Relative weight loss (%)
#1-2	MF-5	50–100	3.40	2.59	23.8%
#1-2	MF-5	50–100	1.18	0.87	26.3%
#1-2				**Mean**	**25.0%**
#1-2	MS-3	50–100	3.64	3.33	8.5%
#1-2	MS-3	50–100	1.20	1.08	10.0%
				Mean	**9.3%**
#1-2	MS-1	100–150	3.15	3.06	2.9%
#1-2	MS-1	100–150	6.50	6.37	2.0%
#1-2	MS-3	100–150	5.36	5.18	3.4%
				Mean	**2.7%**
#1-2	MS-1	150–200	6.48	6.32	2.5%
#1-2	MS-1	150–200	3.09	3.01	2.6%
#1-2	MS-2	150–200	3.13	3.05	2.6%
#1-2	MS-3	150–200	2.89	2.80	3.1%
				Mean	**2.7%**
#3	DY08-7	212–250	1.50	1.50	0.0%

Table 2. Results of the control tests performed under conditions similar to those of Experiment #1–3, but with water instead of HF, in order to evaluate the minimum weight loss achieved during the washing stage.

#1 and #2, and (ii) the differences in the grain sizes (212–250 μm vs. 50–200 μm).

Together, the control sample results suggest that larger grains are less likely to be affected by weight losses associated with rinsing in our experiments, and that the empirical control data obtained on the larger grain fractions may be considered as more reasonable estimates of the weight loss uncertainties associated with Experiments #1–3.

3.4. Estimates of external surface thickness removal

Grain size analysis of the unetched quartz and K-feldspar samples were performed by static image analyses using a Malvern Instruments Morphologi G3 particle characterization system and Morphologi software 7.41, following the procedure outlined in Duval et al. (2015a). With this technique, 3D particles are captured as high resolution 2D images, from which various size and shape parameters may be derived (e.g., diameter, circularity, elongation, convexity). Among them, the Circle Equivalent (CE) diameter is the diameter of a circle with the same area as the 2D image of the particle. For a given unetched sample, a CE diameter was thus obtained for each particle of the grain population and a mean value and associated error (1 standard deviation) were derived as obtained for each natural sample (see Table 3). The coefficient of variation among the 25 samples overall vary between 8.9% and 14%, except one sample (MS3_100–150 μm) showing a much higher value (48.6%).

Using the mean grain size values and the bulk relative mass loss observed during the three experiments, we calculated the post-etching mean diameter of the grain population of each sample, and estimated the average grain thickness removed by HF etching. The latter is expressed as half of the difference between the pre- and post-HF etching mean diameter. This calculation is based on two major assumptions: (i) the grains have a spherical shape, and (ii) they experienced isotropic and uniform removal of their exterior surfaces during the etching process (Bell & Zimmerman, 1978).

Associated uncertainties on the removed thickness values were derived from a combination of the experimental error on the weight loss estimates (i.e., 3% for 100–200 μm and 9% for 50–100 μm grain size fraction in experiments #1 and #2, and 0% for the K-feldspar samples of experiment #3; see Table 2) and the standard deviation on the mean diameter of a given sample (Table 3).

4. Results

4.1. Weight loss estimates

The following observations can be made from experiments #1, #2 and #3 (numerical values are given in Tables 4, 5, 6 and 7):

Experiment #1

- The feldspar sample (MF5) is more significantly affected by HF (10 or 40%) etching in comparison to the quartz minerals (MS1 to MS3), as would be expected. The 10% HF etching experiments conducted on the 100–150 μm grain size fractions (Table 5) produce a relative weight loss of 24.0% (10 min) to 45.1% (60 min) for MF-5, while the quartz sample weight losses do not exceed 10% (10 min) to 20% (60 min).

Sample	Nominal sieve opening range (μm)	Mineral	Mean CE diameter (μm)	s.d. (μm)	Coefficient of variation (%)
MS1	50-100	Quartz	125.4	17.5	14.0%
MS1	100-150	Quartz	165.3	21.2	12.8%
MS1	150-200	Quartz	207.5	25.0	12.1%
MS1	200-250	Quartz	289.6	31.7	10.9%
MS1	250-300	Quartz	349.8	34.1	9.7%
MS2	100-150	Quartz	177.8	21.1	11.9%
MS2	150-200	Quartz	223.8	25.6	11.4%
MS3	100-150	Quartz	119.3	58.0	48.6%
MS3	150-200	Quartz	220.2	30.4	13.8%
MF5	100-150	K-feldspar	160.9	21.4	13.3%
MF5	150-200	K-feldspar	223.3	26.3	11.8%
DY08-9	212-250	K-feldspar	276.9	28.1	10.1%
DY08-10	212-250	K-feldspar	281.0	28.6	10.2%
DY08-11	212-250	K-feldspar	300.8	28.9	9.6%
DY08-12	212-250	K-feldspar	302.2	31.2	10.3%
DY08-13	212-250	K-feldspar	284.5	25.3	8.9%
DY08-14	212-250	K-feldspar	289.9	26.9	9.3%
DY08-15	212-250	K-feldspar	289.1	27.8	9.6%
DY08-16	212-250	K-feldspar	285.5	26.5	9.3%
DY08-17	212-250	K-feldspar	292.5	28.8	9.9%
DY08-18	212-250	K-feldspar	302.3	30.1	10.0%
DY08-19	212-250	K-feldspar	308.1	29.5	9.6%
DY08-20	212-250	K-feldspar	305.9	30.1	9.8%
DY08-21	212-250	K-feldspar	293.7	29.9	10.2%
DY08-22	212-250	K-feldspar	285.4	35.3	12.4%

Table 3. Mean CE diameter and associated standard deviations (s.d.) and corresponding coefficient of variation obtained by Static Image analysis for each natural (unetched) samples.

In comparison, 100% of the 100–150 μm feldspars are eliminated after 10 minutes of 40% HF etching (Table 4). Similar results are observed for the 150–200 μm feldspars after 40 minutes of 40% HF etching.

- In general, the various quartz samples exhibit similar etching trends, though some are more impacted by HF treatment (MS3) than others (MS2). The 40% HF etching experiments conducted on the 100–150 μm grain size fractions produce relative weight losses of 7.6% (10 min) to 32.5% (60 min) for MS-2, while MS-3 lost between 20.5% (10 min) to 48.4% (60 min) of its initial weight (Table 4).

- As expected, minerals of finer grain size (100–150 μm) exhibited higher relative weight losses compared to coarser grain sizes (150–200 μm). This is explained by the change in surface area to volume ratio that occurs with changes in grain size. For example, 60 min etching with 40% HF caused relative weight losses of 32.5% (MS2) to 48.5% (MS3) for 100–150 μm quartz grains, and 26.0 (MS2) to 40.9% (MS3) for 150–200 μm quartz grains (Table 4).

- A similar HF experiment performed by Hong (1998) (see table 3.1, p.45) on quartz samples with a mean size of 137.5 μm yielded the following weight loss estimates: 38.5 ± 4.2% and 49.1 ± 1.8% for 40% HF etching performed over 40 and 60 min, respectively. These results are systematically higher, but nevertheless consistent within error, with those from Experiment #1: an average weight loss of 31.7 ± 6.6% and 40.7 ± 7.9% was observed in our experiment when undertaking 40% HF etching over 40 and 60 min, respectively, for samples MS1, MS2 and MS3 (100–150 μm fraction).

Experiment #2

- As observed above, an inverse correlation was also observed between grain size and relative weight loss in

Experiment #1 (HF 40%)				
Sample_ Grain Size (μm)	**Time** (min)	**Initial weight** (g)	**Final weight** (g)	**Relative weight loss** (%)
MS-1_100-150	10	6.35	5.54	12.8%
	20	6.55	5.41	17.4%
	40	6.07	4.03	33.6%
	60	6.07	3.57	41.2%
MS-2_100-150	10	2.25	2.08	7.6%
	20	2.26	1.88	16.7%
	40	2.20	1.66	24.4%
	60	2.24	1.51	32.5%
MS-3_100-150	10	5.23	4.16	20.5%
	20	5.22	3.95	24.3%
	40	5.09	3.20	37.1%
	60	5.23	2.70	48.4%
MF-5_100-150	10	3.38	0.05	98.4%
	20	3.48	0.10	97.1%
	40	3.47	0	100.0%
	60	3.32	0	100.0%
MS-1_150-200	10	6.21	5.54	10.8%
	20	6.41	5.52	13.9%
	40	6.48	5.08	21.6%
	60	6.54	4.35	33.5%
MS-2_150-200	10	6.42	6.02	6.2%
	20	6.46	5.85	9.4%
	40	6.23	5.09	18.3%
	60	6.28	4.65	26.0%
MS-3_150-200	10	2.80	2.34	16.5%
	20	2.84	2.16	24.1%
	40	2.84	1.77	37.6%
	60	2.79	1.65	40.9%
MF-5_150-200	10	4.02	1.05	73.9%
	20	4.10	1.30	68.2%
	40	4.33	0.05	98.8%
	60	4.17	0.03	99.3%

Table 4. Weight loss data derived from Experiment #1 (HF 40%).

Experiment #1 (HF 10%)				
Sample_ Grain Size (μm)	**Time** (min)	**Initial weight** (g)	**Final weight** (g)	**Relative weight loss** (%)
MS-1_100–150	10	3.35	3.18	5.1%
	20	3.22	3.04	5.6%
	40	3.29	3.02	8.2%
	60	3.31	3.01	9.1%
MS-2_100–150	10	1.57	1.55	1.3%
	20	1.57	1.53	2.2%
	40	1.57	1.52	3.2%
	60	1.57	1.51	4.0%
MS-3_100–150	10	2.67	2.48	7.1%
	20	2.69	2.46	8.6%
	40	2.61	2.31	11.5%
	60	2.73	2.34	14.3%
MF-5_100–150	10	2.77	2.10	24.0%
	20	2.84	2.06	27.6%
	40	2.80	1.78	36.3%
	60	2.98	1.63	45.1%
MS-1_150–200	10	3.26	3.23	0.9%
	20	3.32	3.25	2.1%
	40	3.20	3.11	2.8%
	60	3.24	3.06	5.6%
MS-2_150–200	10	3.08	3.06	0.6%
	20	3.02	3.00	0.7%
	40	3.20	3.12	2.5%
	60	3.21	3.12	2.8%
MS-3_150–200	10	2.83	2.68	5.4%
	20	2.81	2.59	8.0%
	40	2.82	2.63	6.8%
	60	2.85	2.54	10.8%
MF-5_150–200	10	3.57	3.03	15.0%
	20	3.84	3.16	17.7%
	40	3.80	2.78	26.8%
	60	3.69	2.57	30.4%

Table 5. Weight loss data derived from Experiment #1 (HF 10%).

Experiment #2, with higher grain sizes displaying lower relative weight losses (Table 6). For instance, to achieve a 25% relative weight loss for 50–100 μm, 150–200 μm and >200 μm quartz grain sizes, it was necessary to undertake 40% etching for 10 min, 25 min and 40 min, respectively.

- As with Experiment #1, the results of Experiment #2 show that there may be some differences in weight loss depending on the quartz sample under consideration. In this case, sample MS3 is consistently affected by HF etching to a greater extent than sample MS1 (Table 6).
- Three samples were used in both Experiments #1 and #2 (MS1_100–150 μm, MS1_150–200 μm and MS3_150–200 μm). The comparisons of these results (Table 4 and 6) show that, for a given sample, the weight loss after 10 mins of etching is virtually the same in each experiment, but the difference in weight loss significantly increases with time. Relative weight loss systematically exceeded 50% for these samples in Experiment #2, whereas it did not exceed 50% for the corresponding samples tested in Experiment #1. Such a difference could be intuitively expected, although it has never been

Experiment #2 (HF 40%) – with constant agitation				
Sample_ Grain Size (μm)	**Time** (min)	**Initial weight** (g)	**Final weight** (g)	**Relative weight loss** (%)
MS-1_50–100	10	0.84	0.65	23.2%
	20	0.98	0.64	34.0%
	40	0.94	0.41	56.4%
	60	1.04	0.29	72.2%
MS-1_100–150	10	3.31	2.84	14.3%
	20	3.21	2.37	26.0%
	40	3.31	1.65	50.1%
	60	3.15	0.93	70.4%
MS-1_200–250	10	2.63	2.47	6.1%
	20	2.69	2.38	11.6%
	40	2.70	2.00	26.1%
	60	2.68	1.52	43.2%
MS-1_150–200	10	3.16	2.82	10.7%
	20	3.28	2.63	19.7%
	40	3.18	1.87	41.2%
	60	3.00	1.25	58.3%
MS3_150–200	10	2.78	2.28	18.0%
	20	2.73	1.90	30.3%
	40	2.75	1.21	56.2%
	60	2.86	0.69	75.8%
MS1_250–300	10	3.05	2.90	5.1%
	20	3.01	2.70	10.3%
	40	3.12	2.37	24.0%
	60	3.08	1.83	40.5%

Table 6. Weight loss data derived from Experiment #2 (HF 40%) with constant agitation.

properly quantified. A couple of causes may be envisaged. During HF experiment #1, the grains formed a layer of a few mm thick in the beaker. Consequently, without agitation there may be significant differences in terms of etching rates between the grains that are located on top of the layer and those positioned within the layer. Grains in the latter category might simply not be fully in contact with the chemical reagent given their compaction. The constant agitation undertaken during Experiment #2 ensures that the total surface area of the grains is in direct contact with the chemical reagent during the entire reaction. In other words, a greater proportion of grains are exposed to more uniform etching conditions during agitation, resulting in higher weight loss estimates. Another explanation could be the local neutralization or depletion of HF in the immediate surrounding of the grains if no agitation occurs, which may slow down or partly buffer the etching effects over the entire duration of the experiment.

Experiment #3 (HF 10%) – 3 × manual agitation and stirring during the etching period				
Sample	**Time** (min)	**Initial weight** (g)	**Final weight** (g)	**Relative weight loss** (%)
DY08-9	10	1.13	0.88	22.1%
DY08-10	10	1.27	0.98	22.8%
DY08-11	10	1.23	0.93	24.4%
DY08-12	10	1.20	0.92	23.3%
DY08-13	10	1.09	0.83	23.9%
DY08-14	10	0.80	0.53	33.7%
DY08-15	10	0.52	0.40	23.1%
DY08-16	10	0.58	0.42	27.6%
DY08-17	10	0.68	0.52	23.5%
DY08-18	10	1.21	0.94	22.3%
DY08-19	10	1.01	0.78	22.8%
DY08-20	10	0.89	0.70	21.3%
DY08-21	10	1.01	0.77	23.8%
DY08-22	10	1.08	0.83	23.1%

Table 7. Weight loss data derived from Experiment #3 (HF 10% during 10 min).

Experiment #3

- On average, the net dry weight of the fourteen K-feldspar samples was reduced by 24.3% after 10% HF etching for 10 minutes. The weight loss values observed for individual samples is fairly consistent, ranging between 20–25% for all but two of the fourteen samples (Table 7). The remaining two samples display slightly higher weight losses of up to 34%, highlighting that inter-sample variability exists for this geographic location. The weight losses observed for the fourteen K-feldspar samples in Experiment #3 are broadly similar to those observed for K-feldspar sample MF5 in Experiment #1, which was conducted under similar experimental conditions (MF5 weight losses = 24% for 100–150 μm grains and 15% for 150–200 μm grains).

4.2. Removed thickness estimates

The weight loss results have been converted into estimates of removed thickness as indicated in section 3.4. Results are graphically displayed in Figures 2 (Experiments #1 and #2) and 3 (Experiment #3). The corresponding numerical values are given in the Supplementary Information (Table S1 to S4).

4.2.1 Identifying external factors influencing etching rates

As would be expected, the grain thickness removed by HF etching increases almost linearly with time. When us-

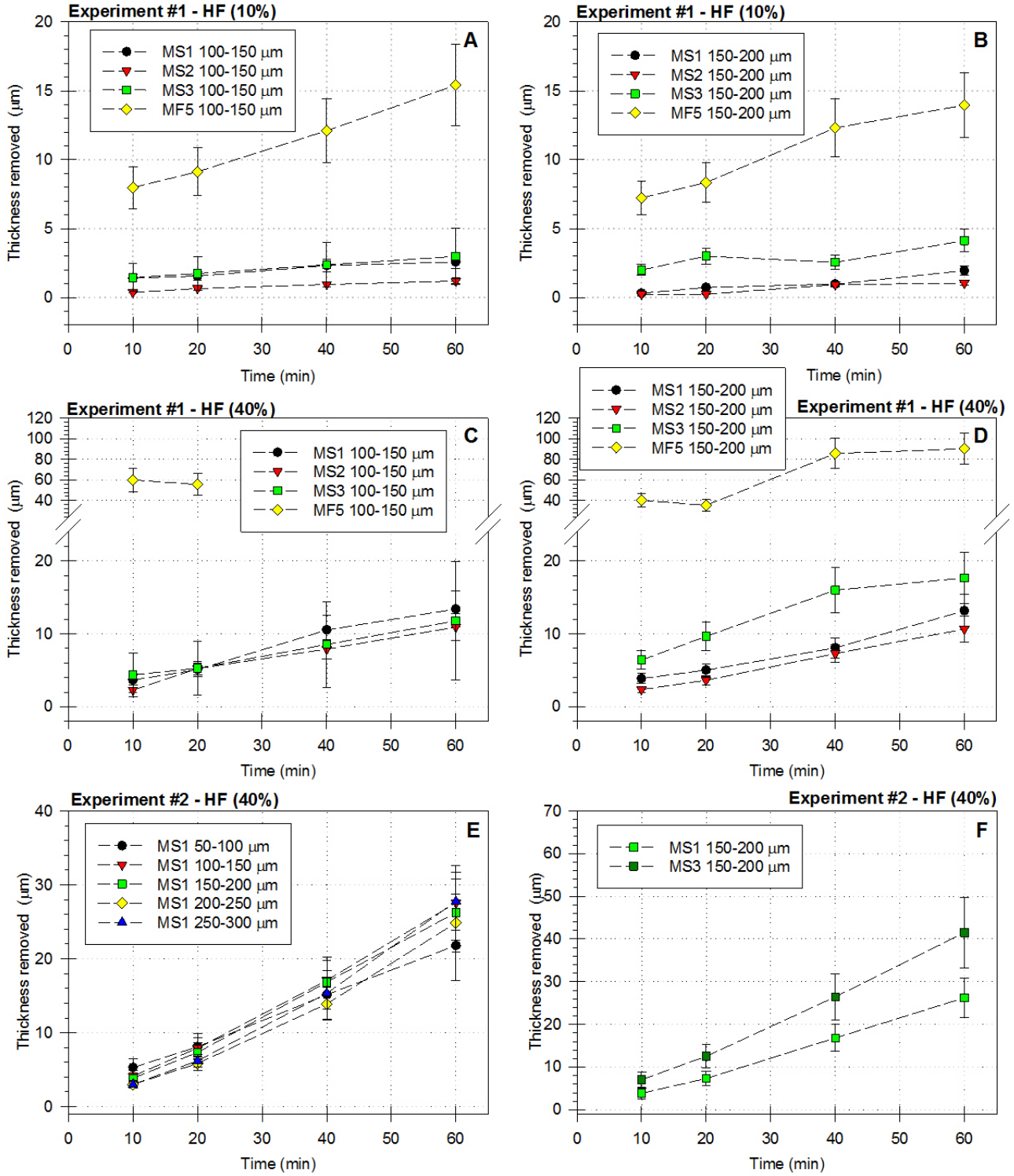

Figure 2. Relationship between grain thicknesses removed from quartz and feldspar samples and HF (10% and 40%) etching duration for Experiments #1 (A to D) and #2 (E and F).

ing 40% HF, the average etching thicknesses ranged from 3.8 ± 1.5 µm after 10 min to 12.9 ± 2.6 µm after 1 hr for 100–200 µm quartz samples (Fig. 2C, Table 8). In contrast, a significantly smaller dependency is observed between etching thickness and time when using 10% HF; grain thickness removal increases by only a factor of ∼2.3 over 10 min to 1 hr etching times (Fig. 2A). After 60 min, 10% HF has only removed a mean external thickness of 2.3 ± 1.2 µm from the quartz grains.

As expected, 40% HF has a more significant impact on

Mineral	Quartz	Quartz	Quartz	K-feldspar	K-feldspar	K-feldspar
Experiment	#1	#2	#1	#1	#1	#3
HF concentration	40% HF	40% HF	10% HF	40% HF	10% HF	10% HF
Sample size	n=6	n=6	n=6	n=2	n=2	n=14
Time (min)						
10	3.8 ± 1.5 µm (39.6%)	4.4 ± 1.5 µm (35.3%)	1.0 ± 0.8 µm (77.3%)	50.2 ± 14.0 µm (28.0%)	7.6 ± 0.5 µm (6.9%)	12.9+1.8m (14.3%)
20	5.7 ± 2.1 µm (36.2%)	8.0 ± 2.4 µm (30.0%)	1.3 ± 1.0 µm (75.3%)	45.5 ± 14.3 µm (31.4%)	8.7 ± 0.5 µm (6.3%)	-
40	9.7 ± 3.3 µm (33.6%)	17.5 ± 4.6 µm (26.2%)	1.7 ± 0.8 µm (47.6%)	85.8 ± 14.5 µm (16.9%)	12.2 ± 0.1 µm (1.2%)	-
60	12.9 ± 2.6 µm (19.9%)	28.3 ± 6.8 µm (24.2%)	2.3 ± 1.2 µm (50.2%)	90.4 ± 15.3 µm (16.9%)	14.7 ± 1.0 µm (7.0%)	-

Table 8. Average removed thicknesses and associated standard deviation (in parenthesis, the corresponding coefficient of variation) evaluated from the weight loss estimates of all samples and grain size fractions considered in each experiment (#1, #2 and #3). To obtain the post-etching grain diameter, the thickness values should be multiplied by two and then subtracted from the initial grain diameters displayed in Table 3. Key: n = number of samples considered for the mean value.

quartz grains than 10% HF, removing external layers that are 4–6 times thicker over 10 and 60 min etching periods (Fig. 2A to D). The results of Experiment #2 confirm that constant agitation of samples has a direct influence on etching rates when using 40% HF. For example, sample MS1 experienced mean grain thickness losses of 3.7 to 13.4 µm for 10 and 60 min etching durations in Experiment #1 (no agitation), whereas equivalent losses of 4.1 to 27.6 µm were observed over the same etching time ranges in Experiment #2 (constant agitation) (Fig. 2C and E). The differences between the results of Experiments #1 and #2 increase significantly over longer etching times; mean grain thickness removals are 12% higher in Experiment #2 compared to Experiment #1 after 10 min, and they are 106% higher in Experiment #2 compared to Experiment #1 after 60 min.

In summary, these empirical results show that experimental conditions have a significant impact on etching rate and magnitude. Though the influence of etching time and HF concentration has already been demonstrated in several previous studies, the role of agitation has, to our knowledge, not been explicitly reported or thoroughly evaluated so far.

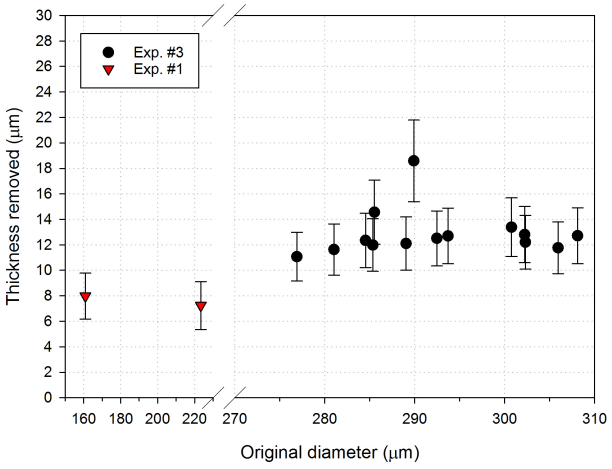

Figure 3. Variability of grain thickness removal from K-feldspar samples derived from Experiment #3. For comparison, data obtained from sample MF-5 during experiment #1 under somewhat similar conditions (HF 10%) are also displayed.

4.2.2 Variability among quartz and K-feldspar samples

Variability in etching effects among different quartz samples is best illustrated by Fig. 2D. For the 150–200 µm quartz samples considered in Experiment #1, MS3 experiences more significant etching losses compared to MS1 and MS2 over 10–60 min etching times. The latter two samples exhibit broadly similar etching thicknesses (within error) over the same time periods. For all three samples, thickness removals range from 2.4 to 6.4 µm after a 10 min etching duration, to 10.7–17.7 µm after 60 min of etching. The same variability in etching magnitude between samples MS-1 and MS-3 is observed in Experiment #2 (Fig. 2F).

In contrast with our previous observations on weight loss estimates, initial grain size appears to have no significant impact on mean removed thicknesses: Experiment #2, which was performed on 50–300 µm (nominal sieve size) grains of sample MS1, reveals consistent mean thicknesses (within error) for all grains size fractions after a given etching time (Fig. 2E). Similarly, 100–150 µm and 150–200 µm K-feldspar fractions of samples MF5 show similar etching thicknesses when using 10% HF for different durations (Fig. 2A and B).

Given these observations, we have calculated average etching thickness values and associated standard deviations

for a given experiment based on a combination of all the samples and grain fractions analysed in each of Experiments #1, 2 and 3 (Table 8). The coefficients of variation for the quartz samples (n=6) analysed during Experiments #1 and #2 range from ∼20% to ∼77% (the reliability of the equivalent values obtained for the K-feldspars are considered relatively uninformative given the limited number of samples considered, n=2). Interestingly, one may observe that very high coefficients of variation are seen when etching is limited (10–20 min). All samples show a common pattern of a decreasing variability with time, with overall minimum values achieved in the range of 20–35% for 40 and 60 minutes. This may be explained by the increasing elimination of the finer grain population with time, resulting in a narrower grain size distribution.

Overall, these coefficient of variation data provide useful insights into inter-sample variability of etching rates, which incorporates both experimental uncertainty (from the washing and weighing stages; though the latter is likely minimal) and inherent variability related to mineralogical maturity, composition, geological origin and grain-to-grain heterogeneities. Based on the present results, the intrinsic relative uncertainty on removed thickness for etched quartz grains is likely to be at least 20% after 40–60 min for a given set of experimental conditions, and can be as high as ∼35% (Table 8).

The variability in etching thicknesses between K-feldspar samples is best observed from Experiment #3 (Fig. 3). The 14 samples considered in this experiment exhibit a mean reduction in grain thickness of 12.9 ± 1.8 µm after etching with 10% HF for 10 min (Table 8). The combined dataset has a coefficient of variation of 14.3%, which is lower than that measured for the quartz samples in Experiments #1–2 (between ∼20% and ∼77%). Given that all 14 K-feldspar samples were collected from a single site, this dataset may provide useful first order constraint on etching rate variability for samples of shared geographic origin. Some variability exists between the etching thicknesses observed in Experiments #1 and #3 for different K-feldspar samples. The K-feldspar removal thicknesses derived from Experiment #1 are smaller (7.6 ± 0.5 µm on average) than those obtained in Experiment #3 (Fig. 3 and Table 8). This difference may reflect differences in the experimental conditions (e.g., different initial sample weights, different agitation and stirring procedures employed in the two experiments), inter-sample variability in K-feldspar etching rates, or, most likely, a combination of both factors.

5. Discussion

5.1. Comparison with previously published results

The majority of luminescence and ESR quartz dating procedures utilise concentrated (40–48%) HF etching for either 40 min or 60 min durations. These various combinations are adopted on the assumption that they would be sufficient to remove a ∼10 µm thick layer from the exterior surface of quartz grains, in accordance with the results from Bell & Zimmerman (1978) and Fleming (1969), respectively. In reality, the weight loss experiments carried out by Bell & Zimmerman (1978) on two different quartz samples revealed more complex results: while one quartz sample that was immersed in 40% HF for 40 min showed an average depth loss of ∼10 µm, the other sample was significantly less affected by the same etching procedure (∼3 µm). These results underscore the inter-sample variability observed in our own experiments. Aitken (1985) mentions the results of a similar HF etching experiment performed on quartz samples by Fleming (1969), for which a ∼9 µm removal was observed after 60 min of 40% HF exposure. This result is likely compatible with the ∼10 µm loss recorded after 40 min by Bell & Zimmerman (1978), as the associated empirical uncertainty of these two experiments was not reported. By comparison, the etched thicknesses obtained in the present study from Experiment #1 (40 min and 60 min exposure to 40% HF) are 9.7 ± 3.3 µm and 12.9 ± 2.6 µm, respectively (Table 8). These results are consistent with the published estimates mentioned above, as well as with those reported by Hong (1998) (i.e., 10.3 ± 1.9 µm and 13.8 ± 1.4 µm for 40 and 60 min of 40% HF, respectively). However, it is worth keeping in mind that mean removed thicknesses were almost twice as high over the same time range when the samples were continuously agitated during HF etching (Experiment #2; see Table 8).

In contrast with quartz dating procedures, there appears to be less standardisation in HF etching procedures adopted in K-feldspar luminescence studies, although there is an apparent overall consensus to avoid the use of concentrated HF (> 40%), even for short durations. Some luminescence practitioners prefer not to include a HF etching step during sample preparation (Duller, 1992; Trauerstein et al., 2014), while others use various combinations of dilute (10%) HF over relatively short etching durations (typically 10 min to 40 min) to remove the outer alpha-irradiated layers of coarse grains (Mejdahl, 1985; Li & Li, 2011; Demuro et al., 2015). The reasons behind these choices of experimental conditions, and especially the different durations, are not always stated (but see Duller, 1992, section 3.2.2.), and they are most likely based on individual laboratory recipes and unpublished studies. Indeed, quantitative assessments of K-feldspar etching rates are scarce in the literature. Porat et al. (2015) reported a decrease in the modal size of 50 and 100 µm K-feldspar grains after 20 and 40 min of exposure to 10% HF, respectively. Consequently, they considered that 10% HF etching for 10-15 minutes should be sufficient to remove most of the outer surface affected by alpha particles. In contrast, longer durations would favour further etching anisotropy for a given grain (see also Duller, 1992) and etching heterogeneity among grains, resulting thus in additional complications and increased uncertainty for dose rate evaluation. We have observed an average K-feldspar depth loss of 12.9 ± 1.8 µm after 10 min etching with 10% HF for 14 samples in Experiment #3 (Table 8), which is consistent with the observations of Porat et al. (2015). However, Experiment #1 also

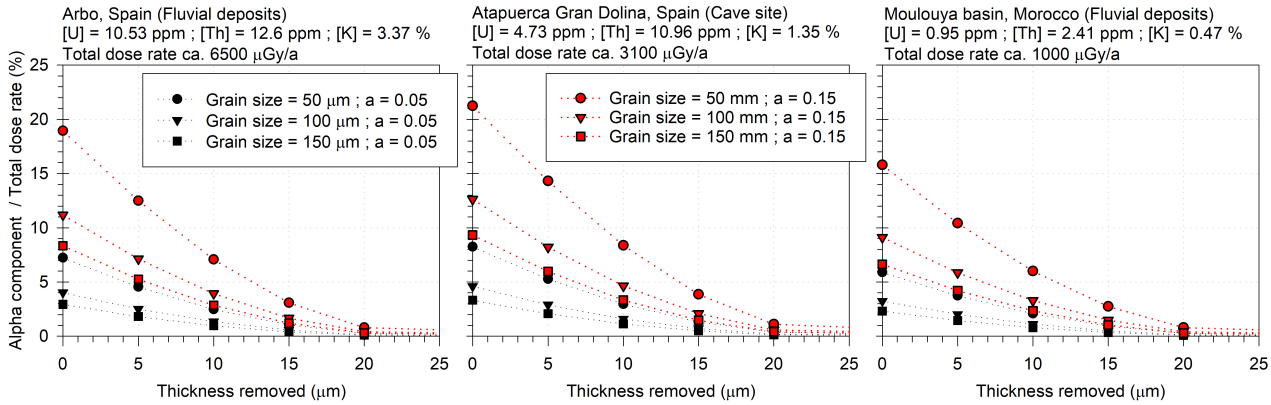

Figure 4. Relationship between relative alpha dose rate contributions (relative to the total dose rate) and assumed HF etching depths for quartz of initial grain size of 50, 100 and 150 µm and an alpha efficiency of 0.05 and 0.15. Three existing case studies are displayed from left to right (in decreasing order with respect to the magnitude of the total dose rate): Arbo (Spain), Atapuerca Gran Dolina (Spain) and Moulouya basin (Morocco). Calculations were performed using the following parameters: internal dose rate = 30 µGy/a, cosmic dose rate = 110 µGy/a, water content = 10% wet weight (equivalent to 11% dry weight), and water correction factors, alpha and beta attenuations, and etching depth corrections from the DRAC data compilation spreadsheet (Supplementary material from Durcan et al. (2015)).

showed lower K-feldspar etching depths of 7.6 ± 0.5 µm for an additional sample. Taken together, 10% HF for 10 min seems to be sufficient to remove the targeted alpha-affected outer ~ 10 µm rind of most coarse K-feldspar grain fractions considered so far; though additional empirical data is needed to better characterise inter-sample variability in K-feldspar etching efficiencies.

5.1.1 Minimum recommended HF etching depth

Although the maximum penetration range of alpha particles in silicate grains is usually considered to be ~ 20 µm, the attenuation factors provided by Bell (1979) show that such an etching depth would not entirely remove the external alpha dose rate component ($\sim 96\%$ would be eliminated). Etching depths of 15, 10 and 5 µm would remove ~ 85, ~ 66 and ~ 38 % of the external alpha dose rate component, respectively. Consequently, it is worth considering whether the 10 µm etching depth usually targeted in ESR and luminescence dating is sufficient to reduce the alpha dose rate contribution to negligible levels in comparison with the total dose rate. Simulations performed by Bell (1979) suggest that a 9 µm etching depth would reduce the external alpha dose rate component to between 2 and 10% of the total dose rate, depending on the alpha efficiency selected (0.05–0.1) and the relative concentration of potassium in the sediment (0 to 2% K_20). For comparison, we ran a series of simulations with three quartz samples collected from different localities (Arbo and Atapuerca Gran Dolina, Spain and the Moulouya basin, Morocco) that contain low to high radioactivity deposits (1,000 to 6,500 µGy/a). In each simulation we considered different grain sizes (50 to 150 µm) and alpha efficiency values that encompass those commonly used in luminescence and ESR dating, (0.05 and 0.15, respectively; e.g. Arnold et al. (2014); Duval et al. (2015b)) (Fig. 4). Our results show that, in all but one extreme scenario (50 µm grain size and alpha efficiency = 0.15), a 5 µm etching depth is sufficient to reduce alpha dose rate contributions to $<10\%$ of the total dose rate. The alpha dose rate contributions are further reduced to $<5\%$ and $<2.5\%$ of the total dose rate for 10 µm and 15 µm etching depths, respectively. Though relatively small, these alpha dose rate contributions may be non-negligible, and it may be worth considering an additional alpha dose rate term as part of the ESR and luminescence age calculation when etching depths are <15 µm.

Although use of increasing HF etching times may be considered as an alternative means of reaching a depth removal >15 µm and thus completely eliminating alpha dose rate contributions, this approach is likely to raise additional problems, as outlined by Bell & Zimmerman (1978). In particular, more stringent HF procedures are likely to increase inter-grain etching heterogeneity and they cannot guarantee that external alpha contributions will truly be removed from all grains. Consequently, Aitken (1985) and Bell & Zimmerman (1978) consider HF removal of the outer 10 µm of silicate grains to represent the most reasonable compromise for dose rate evaluation.

6. Conclusion

Quantification of HF etching effects is essential for the evaluation of the alpha and, to a lesser extent, beta dose rate components in ESR and luminescence dating. Etching thicknesses ranging from 0 to 20 µm have relatively limited impact on the resulting beta dose rate of quartz grains ($<2\%$), whereas the alpha dose rate may be reduced by up to 96% (see Aitken, 1985). Building on the earlier work of Fleming (1969) and Bell & Zimmerman (1978), which still stand as references in luminescence and ESR dating, our study provides additional, detailed empirical data highlighting the variability of etching rates as a function of experimental conditions and sample type. Based on our results, the outer

10 µm rind of quartz samples (i.e., the usual target in ESR and luminescence dating studies) can be removed by etching with 40% HF for 40 min when including periodic manual agitation, or by etching with 40% HF for $\sim$20 min when undertaking continuous agitation. For K-feldspars, etching with 10% HF for between 10 and 40 min was required to remove the outer 10 µm rind of the samples considered in this study. These results are in good agreement with previous etching assessment studies, although we recommend that each laboratory evaluates etching thickness losses (and associated empirical uncertainties) for their specific HF experimental setup given the observed variability of etching rates. HF etching depths of between 5 and 15 µm will significantly reduce external alpha dose rate contributions to <2.5 – <10% of the total dose rate (depending on the alpha efficiency value used). Although relatively small, this contribution is nevertheless non-negligible. Consequently, it may be worthwhile to consider an additional alpha dose rate term as part of the ESR and luminescence age calculation when etching depths are <15 µm.

Finally, the reliability of HF etching depths based on weight loss estimates is directly dependent on the validity of two important assumptions, i.e. the spherical shape of the grains, and isotropic HF etching of individual grains, as well as collective grain populations, for a given sample. Although these assumptions are known to be oversimplistic (e.g., Bell & Zimmerman, 1978; Goedicke, 1984; Duval et al., 2015a), their true impact on the accuracy of empirical etching depth calculations remains unstudied and largely unconstrained. Preferential dissolution has been observed along crystallographic directions (e.g., Tellier & Jouffroy, 1983), fissures and grain boundaries (Porat et al., 2015), systematically inducing uneven etching at both single-grain and multi-grain scales (e.g., Duller, 1992), which may sometimes result in grain disintegration. The magnitude of HF etching among different grains of a given sample may significantly vary, with potentially non-trivial implications for single-grain OSL dating studies. In that regard, comparative assessments of standard weight loss assessments with different quantitative approaches such as Static Image Analysis (Duval et al., 2015a) and Laser Diffraction should enable further insights into the impact of uneven HF etching at both single and multi-grain levels.

Acknowledgments

This study received funding from Australian Research Council Future Fellowship FT150100215 and FT130100195. MD would like to thank M. Bartz (University of Cologne, Germany) for sharing the data of a sediment sample from the Moulouya basin (Morocco). Finally, the constructive comments by G.A.T. Duller and an anonymous reviewer on an earlier version of the manuscript have contributed to improve the quality of this work.

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Reviewer

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