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Methods Note: Can hydrogen peroxide digestion of organic matter ever be too aggressive for OSL dating?

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1. Introduction

Removal of organic matter and digestion of organic residues is a ubiquitous step in sample processing for luminescence dating (Aitken, 1998). Macroscopic organic debris, if present, is largely captured during grain-size sieving. Most, if not all, laboratories use a hydrogen peroxide (H_2O_2) treatment to digest microscopic organic debris and organic residues. It is not uncommon for samples, even samples collected from C-horizons, to react mildly or moderately to H_2O_2 at reagent concentration (30% solution) for a period of up to a few hours. Occasionally samples are encountered that react rapidly and vigorously to H_2O_2 or, conversely, samples that seem to have a delayed reaction; not reacting immediately but after several hours of soaking in H_2O_2. The collective experience of numerous luminescence dating labs indicates that these "normal" reactions to H_2O_2 treatment do not have a significant impact on the resulting measured TL/OSL signals or D_e distributions; thus the ubiquitous use of H_2O_2 digestion.

Recently we processed a set of samples that reacted so intensely and for such a prolonged period that we questioned, *"Can H_2O_2 digestion of organic matter ever be too aggressive for OSL dating?"* One of the samples provided an opportunity to experimentally evaluate that question. The sample set comes from a strandplain (or ridge and swale) shoreline sequence bordering Lake Claire in northeastern Alberta, Canada. Tar sands are mined in this region and notably so upstream along the Athabasca River. However, based on the estimated ages of the samples and geomorphological interpretations, it was not anticipated that significant amounts of tar sands would have been incorporated into the ridges that were sampled (Zamperoni et al., 2017). Even if the samples did contain some sand grains and/or bitumen derived from the tar sand deposits, it still must be removed and H_2O_2 treatment is the standard.

2. Treatments and Observations

It is important to state that the personnel conducting the treatments described herein all had received university level chemical safety training as well as luminescence dating laboratory specific safety training. The recommended PPE was worn at all times and the HF treatments described later were conduct in an HF compliant fume hood and with a safety spotter monitoring at all times.

In our laboratory we generally treat 10 – 20 cm^3 of sieved sediment with 25 – 50 ml of 30% H_2O_2 solution. The first two Lake Claire samples processed reacted very vigorously with H_2O_2 and required spent solution to be decanted and fresh H_2O_2 to be introduced at least twice. Although the reactions were vigorous and somewhat prolonged, they were not exceedingly beyond past experiences, so the reactions were noted on a sample data sheet and work proceeded to the third sample.

When H_2O_2 was added to the third sample the initial reaction was shockingly violent with profuse bubbling and prodigious emission of gas for both the 90 – 150 µm and the 150 – 250 µm size fraction. The reaction was slowed/cooled by adding DI water. When the reaction subsided the solution was decanted and fresh H_2O_2 added. The reaction immediately resumed its former violence. At this point the sample was placed in a reaction safe cabinet and allowed to spend the available H_2O_2. The H_2O_2 was refreshed twice a day for 4 days. Each time the spent solution was decanted, it was milky or silty, even though prior to adding fresh H_2O_2 we would rinse the sample in DI water until the decanted water was clear. During the four days of decanting and adding fresh

H_2O_2 we took a subsample out of the OSL lab where it could be examined under normal lighting and indeed there were black sand-sized grains present. Although these can typically be seen under lab lighting, it is not uncommon for beach deposits to contain grains of biotite, amphibole, or magnetite. So, the presence of a small proportion of black grains was not considered unusual at the start of the project. Additionally, on the fourth treatment day the reaction had slowed to a level where we could visually see the top and sides of the beaker. We noticed that gas was being released from discrete foci throughout the sediment and traveled toward the surface in vertical bubble streams or jets where they erupted (see supporting video). Our interpretation of the various observations during processing of this sample is that it did include a proportion of sand-size particles that were aggregates of smaller particles cemented by bitumen and likely sand grains with bitumen surface coatings as well. The most likely source of these particles and grains is erosion of tar sands far prior to industrial activities in the region.

To evaluate the impact of the H_2O_2 processing we created subsamples or batches in the 90 – 150 µm (VFS) and 150 – 250 µm (FS) size-fraction that were treated in different manners. Batch 0 (FS) was the original sample that spent over 4 days in twice daily refreshed 30% H_2O_2 solution. Batch 1 (VFS) were treated as normal by direct digestion in the H_2O_2 solution for ~16 hours. Batch 2 (VFS) was mechanically disaggregated prior to H_2O_2 treatment. Batch 3 (FS) samples were treated with Acetone to dissolve bitumen.

Batch 2 samples were placed in a very low concentration (5 mmol) solution of sodium pyrophosphate dispersant with a magnetic spin bar. It was agitated with the spin bar in this solution for ~16 hours to promote break down of bitumen cemented fine-grained aggregates. Of course, the supernatant liquid was very cloudy or milky. The sample was rinsed in DI water until the decanted rinsate was clear. Fresh dispersant solution was added and the sample was again agitated with the spin bar for an additional 8 hours. At this stage the supernatant liquid was only slightly cloudy. The sample was rinsed and we proceeded to a standard H_2O_2 treatment (30% solution). The reaction was vigorous, but significantly subdued compared to batch 0 and 1.

Batch 3 was treated with 90% acetone and agitated with a magnetic spin bar for ~16 hours. After this treatment the solution (waste acetone) was extremely dark in appearance. The sample was rinsed in fresh acetone twice, after which the rinsate was essentially clear. No additional treatments for organic removal were conducted on batch 3.

Following these treatments for organic matter all grain-size fractions were processed in the same manner to obtain clean quartz for OSL measurement (HCl, HF, post-HF rinses; see supplement to Lepper et al. 2007 for details). All sample batches in this study reacted vigorously with HF generating noticeable heat and gas. One might expect that batch 1, because of a shorter H_2O_2 treatment, may have reacted much more vigorously with HF than the other batches. However, based on our observations, that was not the case.

The prepared sand from all batches was measured using a Risø DA-15 TL/OSL reader system. The system is equipped with a 40 mCi 90Sr/90Y ß-source for dose calibrations, which irradiated at a rate 0.113 Gy/s at the time of the experiments. Luminescence was stimulated with blue light (470 ± 30 nm) from a diode array and measured with an EMI model 9235QA PMT in the UV emission range (5 mm Hoya U-340). OSL SAR data collection procedures were used (Murray & Wintle, 2000) with a uniform cut heat and preheat of 160 °C for 10s throughout the SAR process (Lepper et al., 2000; Wintle & Murray, 2006). The SAR procedures used included four regeneration doses. Dose response calibration was conducted for every aliquot and it was linear within the regeneration dose range used. Ninety-six (96) individual aliquots were analyzed from each batch in this study. Prepared aliquots have been estimated to contain approximately 300 grains. Data was mildly filtered following the criteria described in Lepper et al. (2003; 2007 supplement) resulting in D_e data sets ranging from n = 94 to 96 aliquots for analysis and comparisons.

Table 1. Summarized conditions and results of this study.

Batch ID - grain size	**Organic Removal Treatment**	**n**[1]	**M/m**^{2}	ν_t[3]	**Data Mean D_e (Gy)**	**Freq. Dist. Mean D_e (Gy)**
Batch 0 - FS	Over 96 hour soak in 30% H_2O_2	94/96	1.01	11.10%	12.95 ± 0.15	12.97 ± 0.09
Batch 1 - VFS	~ 16 hour soak in 30% H_2O_2 (control)	94/96	1.01	10.50%	13.11 ± 0.14	13.01 ± 0.14
Batch 2 - VFS	24 hours continuous aggitation in dispersant prior to 16 hour soak in H_2O_2	96/96	0.97	13.50%	12.74 ± 0.18	13.06 ± 0.24
Batch 3 - FS	~ 16 hour continuous aggitation in Acetone; no H_2O_2	95/96	0.98	12.40%	13.06 ± 0.17	13.06 ± 0.19
Mean ± group std. dev.					**12.98 ± 0.18**	**13.03 ± 0.05**

[1]No. of aliquots used for OSL De calculation / no. of aliquots from which OSL data was collected (filtering criteria given in Lepper et al., 2003)
[2]Mean/median ratio: a measure of dose distribution symmetry/asymmetry (see supplement to Lepper et al., 2007).
[3]Total dose distribution data dispersion (Std. dev./mean).

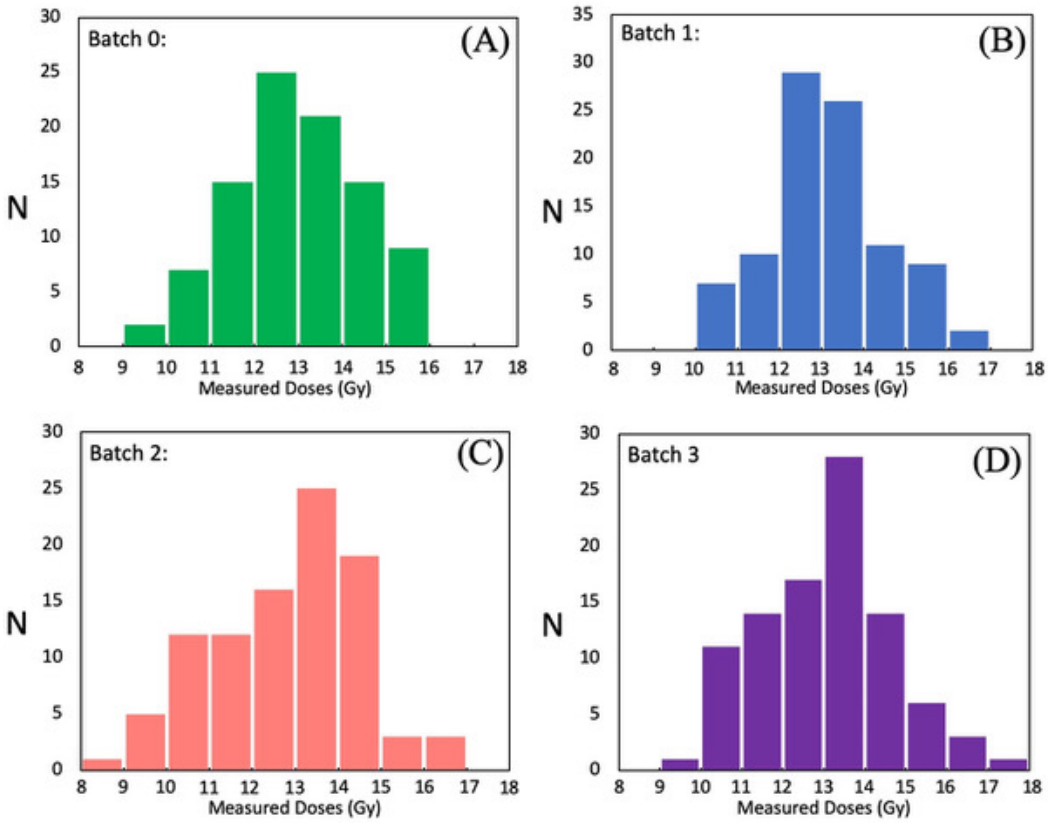

Figure 1. D_e data histograms for each treatment group/batch (A) Over 96 hour soak in H_2O_2 (B) ~ 16 hour soak in H_2O_2 (C) ~ 16 hours of agitation in dispersant prior to H_2O_2 (D) ~ 16 hours of continuous agitation in acetone; no H_2O_2 treatment.

3. Results

Table 1 shows the treatment groups for which OSL SAR measurements were made, the organic removal treatment received, the mean and std. err. of the individual D_e data sets that were derived from both the data and from fitting the data with a single Gaussian population model, as well as some additional parameters that our lab uses to characterize or evaluate dose distributions. Figure 1 shows the D_e data histograms for each batch and Figure 2 shows the derived frequency distributions from the Gaussian models for the treatment groups. As can be seen there is virtually no difference among the treatments and no statistically significant difference in mean D_e among the treatment groups evaluated (Table 1). All D_e distribution means are within one 1 std. dev. of their group mean when considering their respective errors.

Batch 1, which had no agitation and the shortest H_2O_2 soak time, had the lowest data dispersion (ν_t in Table 1) reflected as the narrowest frequency distribution (Figure 2) but, again, it is not statistically significant. The data histogram for batch 2 and to some degree batch 3 have a suggestion of more lower D_e values (Figure 1). Both of these batches underwent an extended period of mechanical agitation during the organic removal treatments. Both of these batches, 2 and 3, also have higher data dispersion (ν_t in Table 1) than batches 0 and 1. Similarly batches 2 and 3 have mean/median ratios (M/m in Table 1) of less than 1.00, which quantifies a slight skew to lower D_e values. A perfectly symmetric distribution has a M/m value equal to 1. However, the differences in these parameters from batch to batch and the difference from ideal behavior is subtle and within normal ranges ob-

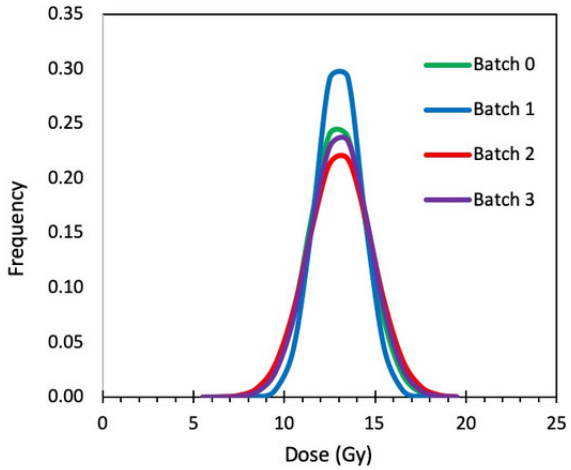

Figure 2. Frequency distributions derived from the Gaussian models for the treatment groups/batches.

served in other projects.

This small experiment also highlights the use of acetone to dissolve oily residues and grain coating from sands. Acetone dissolution could be used as part of the pre-processing of bituminous sands for luminescence dating. However, it may be advisable to develop a procedure that does not require an extend period of mechanical agitation in the acetone.

4. Conclusions

Despite alarmingly vigorous reactions, our data suggests that direct digestion of organic matter with a reagent grade 30% solution of H_2O_2, even for samples containing a noticeable fraction of bitumen, does not result in a significant or deleterious impact on D_e determinations. Although not a statistically robust conclusion, some quantifiable parameters suggest that prolonged periods of stirring in liquid (mechanical agitation) may not be advisable. Acetone may provide an alternative to hydrogen peroxide when removing oily residues and bitumen from sand samples.

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Reviewer

Christina Neudorf

Reviewer comment:

I've wondered about the potential effect of chemical treatments on measured D_e values from sediments. This short methods note shows encouraging results. Several questions could be addressed in a future in-depth study.

I wonder if the exothermic reaction attained during HF treatment of quartz leads to a similar temperature increase of the sample as the H_2O_2 treatments in this study. It would be interesting to know if perhaps a larger difference in measured D_e (or signal intensity) would be observed with and without H_2O_2 treatments, if the sample was not subsequently treated with HF (as is sometimes done with feldspar). Also, more detailed data analysis could show the effect the various treatments have on signal sensitivity. If sample treatments do lead to changes in signal sensitivity, this may have an impact on signal counting statistics, dose distributions and final D_e error.