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Pretreatment of Nitric Acid with Hydrogen Peroxide Reduces Total Procedural Os Blank to Femtogram Levels

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ABSTRACT: Determining and correcting for background contributions of Re and Os from chemical reagents is critical for accurate and precise Re−Os dating of materials with parts per billion to parts per trillion Re and Os concentrations. Here we investigate reducing Os content in nitric acid, as it is the main contributor to the Os blank. Pretreating high-purity nitric acid with hydrogen peroxide (H_2O_2) significantly reduces nitric acid's Os contribution to femtogram levels, greatly reducing Os blank corrections. The improvement in background Os allows analysis of samples with extremely low Os concentrations (into the low ppt level). We present experimental data identifying key factors in reducing Os blank, including nitric acid to hydrogen peroxide volume ratios, wet versus dry glassware, and dark versus lighted reaction environments. These variables affect the reaction time between the two reagents, which in turn correlates inversely with the final Os content. The volume ratio of H_2O_2/HNO_3 is shown to be the fundamental control on reaction time and final Os content, yielding a well-defined exponential relationship; minor variations in reaction time result from wet/dry glassware and light/dark reaction environment. At a H_2O_2/HNO_3 volume ratio of ∼0.24, the total procedural Os blank is reduced from 6.5 pg (no H_2O_2) to 0.043 pg. The $^{187}Os/^{188}Os$ of the Os blank ranges from 0.18 to 0.36, consistent with the Os blank compositions obtained by the AIRIE Program and other Re−Os laboratories worldwide, and is uncorrelated with any experimental variables. In contrast to Os, pretreatment with hydrogen peroxide did not improve the Re blank of nitric acid; Re background reduction requires conventional methods such as sub-boiling distillation.
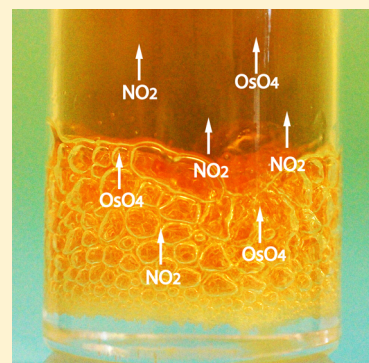
With improvements in chemical separation procedures and mass spectrometric measurements, the past 20 years has seen application of the Re−Os system expand into new geological settings.[1] Re−Os data have been used to constrain the age of ore deposits, meteorites, organic-rich shales, and hydrocarbon systems, and to provide insights on diverse topics such as paleoclimate and mantle geochemistry.[1,2] Most geological samples, with the exception of molybdenite,[3] contain very low Re and Os (ppb to ppt) concentrations,[2] making accurate and precise Re and Os concentration measurements challenging. Therefore, as sample Re and Os become vanishingly low, accurately characterizing and correcting for analytical Re and Os blanks becomes increasingly critical.[4−6] With the exception of black shales, which are typically digested in $H_2SO_4-CrO_4$ solution in order to decompose organic matter and avoid dissolution of detrital silicate minerals,[7−10] most other geological samples, including sulfides,[11,12] native metals,[13] ultramafic rocks,[14] water,[5] bitumen[15] and crude oil,[16] are digested in inverse aqua regia (3 parts HNO_3 + 1 part HCl) or nitric acid. Therefore, it is vital to efficiently reduce the Os content in nitric acid, which is the main source of background procedural Os blank. Available "high purity" single or double-distilled acids cannot be used as Os is actually enriched in the distillation products as OsO_4 is co-distilled.[17] There are no published systematic investigations on improving Os blanks in nitric acid, however, qualitative Os blank reduction procedures have been published.[6,18] Conventional methods to purify nitric acid include sub-boiling distillation in order to remove Os as OsO_4 gas, but this is time-consuming, requires specialized equipment, and can lead to co-distillation of other products.[18] In this paper, we present a fast, efficient, and easily implemented method to significantly decrease procedural Os blanks by purifying nitric acid with concentrated hydrogen peroxide (H_2O_2).

■ EXPERIMENTAL SECTION

Outline of Nitric Acid Purification. Purifying nitric acid using hydrogen peroxide is a simple procedure that does not require special apparatus. Concentrated nitric acid and H_2O_2 are mixed in a precleaned tall quartz (or glass) beaker. A sufficiently tall beaker is required to contain the mixture during eruptive outgassing. The beaker is left undisturbed in a fume hood. The reaction between HNO_3 and H_2O_2 (H_2O_2 + $4HNO_3 \rightarrow O_2 + 4NO_2 + 3H_2O$) initiates as a stream of fine bubbles similar in appearance to champagne. With time, this exothermic reaction raises the temperature of the solution and the rate of bubble formation. The time during which fine bubbles form is referred as the "bubbling step" and can last minutes to hours depending on experimental conditions. Then,

Table 1. Experimental Conditions for Purification of 50 mL of ACS Grade HNO$_3$ by H$_2$O$_2$

	test											
	1	2	3	4	5	6	7	8	9	10	11	12
quartz beaker condition[a]	dry	dry	dry	dry	dry	dry	wet	wet	wet	wet	wet	wet
fluorescent hood lights[b]	off	off	off	off	off	off	on	off	on	off	on	off
added H$_2$O$_2$ (mL)	12	12	9	9	6	6	12	12	10	10	9	9
stirring	yes	no	yes	no	yes	no	yes	yes	yes	yes	yes	yes
reaction time (min)	127	124	54	57	26	25	123	165	66	96	51	70

[a]Dry beaker means the beaker is completely dry at room temperature. Wet beaker means the beaker has been thoroughly wetted by rinsing with Milli-Q water with little water film. [b]Reaction time was monitored with and without hood fluorescent lamp lighting.

Table 2. Total Procedural Re and Os Blanks and Experimental Conditions Using Purified Redistilled Grade HNO$_3$ with H$_2$O$_2$

	run no.						
	LL-745	LL-746	LL-747	LL-748	LL-749	LL-750	LL-751
beaker condition[a]	dry	dry	dry	dry	dry	dry	dry
fluorescent hood lights[b]	off	off	off	off	off	off	off
HNO$_3$ amount (mL)	50	50	50	50	50	50	50
H$_2$O$_2$ amount (mL)	0	4	6	8	9	10	12
H$_2$O$_2$/HNO$_3$ (V/V)	0	0.08	0.12	0.16	0.18	0.20	0.24
reaction time (min)	N/A	19	32	53	64	78	149
Re blank (pg)	3.12	6.50	3.56	2.113	0.562	2.142	6.30
error (2σ)	0.04	0.08	0.04	0.025	0.009	0.025	0.08
Os blank (pg)	6.411	0.59	0.288	0.1774	0.0738	0.1029	0.0433
error (2σ)	0.026	0.04	0.003	0.0021	0.0010	0.0011	0.0008
Os removed (%)	0	90.8	95.5	97.2	98.8	98.4	99.3
^{187}Os/^{188}Os	0.1833	0.894	0.2619	0.2536	0.363	0.3059	0.536
error (2σ)	0.0006	0.023	0.0019	0.0025	0.004	0.0027	0.007

[a]Dry beaker means the beaker is completely dry at room temperature. [b]Reaction time was monitored without hood fluorescent lamp lighting.

almost instantaneously, a vigorous reaction occurs, forming copious O$_2$ and NO$_2$ gas. We refer to this as the "eruption step". Without sufficient beaker height, the eruption may overtop the beaker. Thus, the setup should always include an underlying tray for any spills. The eruption marks the end of the reaction, and no further bubbling is observed. The pale-brown to yellow (from the NO$_2$ gas) HNO$_3$−H$_2$O$_2$ solution is then gently heated on a hot plate to volatilize the NO$_2$ until the solution returns to a colorless state. We refer to this as the "boiling step". After this step, the nitric acid is purified and ready for use in Re−Os geochemistry. In brief, the purification procedure is composed of three steps: bubbling, eruption, and boiling.

On the basis of our previous experiments, both the bubbling and eruption steps are essential to reduce Os background in nitric acid. We have observed that a short reaction time during the bubbling step, less than 1 h, does not significantly reduce Os blank. Similarly, a long reaction time with no eruption also results in a high Os blank. Here, we provide a hypothesis for the nitric acid Os purification mechanism. During the bubbling step, H$_2$O$_2$ reacts with nitric acid to produce fresh O$_2$, a strong oxidizer, which moves Os to its highest oxidation state (Os^{8+}), leading to the formation of OsO$_4$. This process is slow and, therefore, sufficient reaction time is necessary to fully oxidize Os to form OsO$_4$. Although OsO$_4$ is volatile, the small bubbles formed during the first step are inefficient at sparging OsO$_4$ from the solution. The eruption step, which produces abundant O$_2$ and NO$_2$ bubbles in a short time, together with heat from the reaction, helps volatize and liberate OsO$_4$ from the nitric acid. Consequently, the Os blank in nitric acid is improved

significantly only if both steps occur; a prolonged reaction must be followed by an eruption step.

Reaction Time Test at Different Experimental Conditions. To test our hypothesis for Os purification of nitric acid and optimize procedures, we conducted a series of reactions at differing experimental conditions. On the basis of ad hoc reactions performed during routine Re−Os analyses at the AIRIE Program, Colorado State University, we identified the most important variables to be the volume ratio of H$_2$O$_2$:HNO$_3$, the use of wet versus dry quartz beakers to host the reaction, the use of dark versus light hood space during the reaction, and the amount of stirring of the mixture in the quartz vessel. "Dry beaker" means the beaker is completely dry at room temperature. "Wet beaker" means the beaker is wetted and retains a thin water film on the inner wall after being rinsed by Milli-Q water. While intuitively, the volume ratio of H$_2$O$_2$:HNO$_3$ should have the greatest control on Os blank, wet/dry beakers could also affect reaction time. This may result from dilution (minor and unlikely) or film surface processes. Table 1 shows all combinations of tested conditions and the duration of the bubbling step. All experiments kept the nitric acid volume constant at 50 mL of ACS Plus grade 69.4% nitric acid (Fisher Scientific), while increasing volumes of ACS grade 30% H$_2$O$_2$ (from 6 to 12 mL, Fisher Scientific) were used to study reaction time at different experimental conditions. The reagents were mixed in 400 mL quartz beakers, and the duration of the bubbling step was recorded. We observed systematic changes in reaction times depending on the volume ratio of H$_2$O$_2$:HNO$_3$ (Table 1). These results demonstrated different reaction times (Table 1) which should result in

different Os blanks. In other words, we suspect that longer reaction times have lower Os blanks. Hence, a second round of experiments was performed with a better grade of nitric acid Redistilled, GFS Chemicals) to confirm that Os blank correlates with reaction duration. As mentioned previously, a significant reduction in Re blanks is not expected during H_2O_2 purification of HNO_3. However, we did analyze the Re content of the purified acids to double-check this and confirm that we did not introduce external Re in the solutions.

Experimental Procedure for Re and Os Blank Evaluation. We analyzed total procedural Re and Os blanks using inverse aqua regia under the stated experimental conditions (Table 2). A series of seven 50 mL 69% redistilled nitric acid volumes were mixed with 0, 4, 6, 8, 9, 10, and 12 mL of ACS grade 30% H_2O_2 (Fisher Scientific). Total procedural Re and Os blank values were determined by isotope dilution using single [185]Re and [190]Os spikes. The full experimental procedure followed established Re−Os protocols for sulfide samples at the AIRIE Program. Eleven mL of the purified HNO_3 is loaded into a Carius tube sitting in dry ice/acetone slush. Low temperatures prevent loss of any volatile Os species. After the HNO_3 is completely frozen, 4 mL of 22% redistilled HCl (GFS Chemicals) is added to the Carius tube. Then, upon freezing of the HCl, known amounts of the tracer solutions ([190]Os and [185]Re enriched spikes) are added. Upon complete freezing, the Carius tube is sealed, placed in a stainless-steel jacket, and heated for 12 h at 230 °C.[19] The Os is then extracted from the equilibrated solution by solvent extraction with 10 mL of HPLC grade chloroform (Fisher Scientific), and back-extracted into 6 mL of 44−49% HBr (Seastar Chemical Inc.). The Os is further purified from the residual matrix by micro-distillation.[6] The Re is purified using standard anion exchange columns (AG1-X8, 200−400 mesh, chloride form, Bio-Rad Laboratories, Inc.) and single bead "cleanup" (>20 mesh beads from AG1-X8, 20−50 mesh, chloride form, Bio-Rad Laboratories, Inc.). Re and Os fractions are loaded on separate Pt filaments (H. Cross Company, 99.995% Pt) and measured by negative thermal ionization mass spectrometry (NTIMS) on a ThermoFisher TRITON. Re is determined using the total evaporation technique.[20] Os is analyzed by SEM counting in peak-jumping/dynamic mode. Both Re and Os are corrected for oxygen isotopic composition, and Os is corrected for instrumental mass fractionation using a [192]Os/[188]Os ratio of 3.08271.[21]

■ RESULTS AND DISCUSSION

Factors Controlling the Reaction Time. Our results show that the duration of the first bubbling step plays a vital role for oxidization of Os into volatile OsO_4, thereby reducing Os blanks. The most critical factor controlling the duration of the bubbling step is the amount of added H_2O_2 (Table 1 and Figure 1). For each set of experiments, holding other variables constant (e.g., tests 1, 3, and 5; tests 2, 4, and 6; tests 7, 9, and 11; tests 8, 10, and 12), reaction time increased exponentially with the addition of more H_2O_2 (Figure 1). On the basis of previous experience, we have found that at least 1 h reaction time is a threshold to reduce the Os blank to the 100 femtogram level, which is sufficiently low for Re−Os analysis of most geological samples. The reaction time surpasses 1 h only if the amount of H_2O_2 added is more than 9 mL. Turning off fluorescent hood lights extends reaction time by 34%, 45%, and 37% compared to having the lights on (Table 1, compare tests 7 and 8, tests 9 and 10, and tests 11 and 12, respectively).
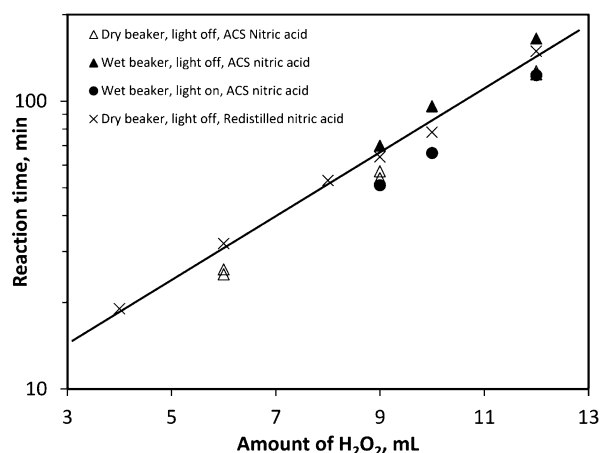

Figure 1. Exponential relationship between amount of added H_2O_2 and the reaction time until eruption.

Additionally, the use of a wet beaker extends reaction time by about 30% compared to the use of a dry beaker (Table 1, compare tests 1 and 8 and tests 3 and 12). In sum, hood lights and beaker condition have a roughly similar influence on the reaction time and may be used to further extend the reaction time for a given volume ratio of H_2O_2:HNO_3. Interestingly, at equivalent reaction conditions (dry beaker and lights off), redistilled nitric acid has consistently longer reaction times than ACS nitric acid (Figure 1). This probably results from impurities in the lower-grade ACS nitric acid that facilitate reactivity, thereby triggering an earlier final eruption and shortened reaction time. Finally, stirring appears to have no effect on the reaction time (Table 1, compare tests 1 and 2, tests 3 and 4, and tests 5 and 6). This suggests that the degree of mixing between HNO_3 and H_2O_2 and facilitation of bubbling have no effect on the reaction time.

Total Procedural Re and Os Blanks. Given the ability to widely vary the H_2O_2−HNO_3 reaction time by adjusting the mixture ratio and environmental conditions, logic dictates that the Os concentration of the reacted nitric acid would also vary. The following results document this.

With addition of H_2O_2 and consequent extension of the reaction time (Figure 2), the total procedural Os blank is
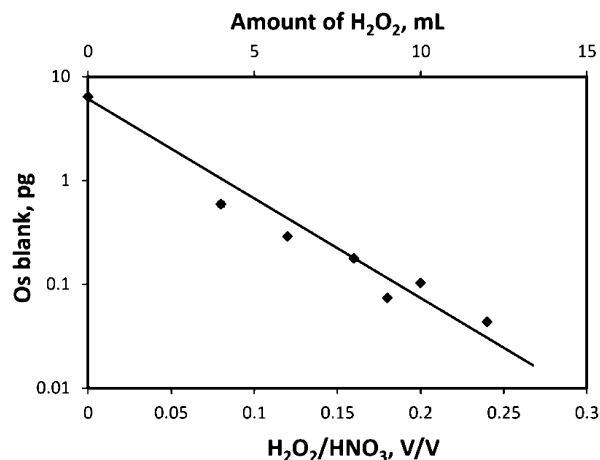

Figure 2. Total procedural Os blank dependence on the amount of added H_2O_2 (for all cases, 50 mL of nitric acid was used). Error bars are smaller than symbol size.

reduced exponentially by 2 orders of magnitude from 6.41 pg (0 mL H_2O_2) to 43 femtogram (12 mL H_2O_2). The 43 femtogram Os blank is the lowest blank we measured from a mixture that still undergoes the "eruptive step". On the basis of our experience, adding more H_2O_2 inhibits the Os-releasing eruptive step and the nitric acid retains a high Os blank. Therefore, we recommend a H_2O_2/HNO_3 maximum volume ratio of ~0.24 to achieve a low Os blank (Figure 2). Our mass balance shows that more than 90% of the Os was removed from redistilled nitric acid when the volume ratio of H_2O_2/HNO_3 was >0.08, and 99.3% Os was removed from redistilled nitric when the volume ratio was 0.24 (Figure 3 and Table 2). The

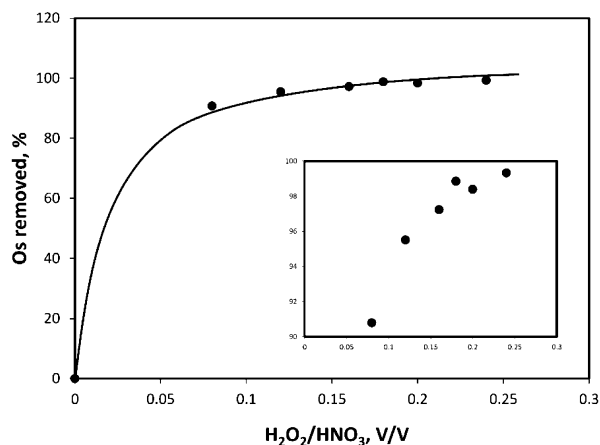**Figure 3.** Percent Os removed from the nitric acid vs H_2O_2/HNO_3 volume ratio.

total procedural Os blank was improved significantly by using different nitric acid sources treated by different amounts of added H_2O_2, which further documents that nitric acid is the main source of Os blank. Furthermore, given the relationship between nitric acid treatment and measured Os blank, it can be presumed that >99% of our total Os analytical blank is derived from the nitric acid (Figure 3). If we assume all Os blank is derived only from nitric acid, our lowest Os blank of 43 pg corresponds to ~2.6 fg g^{-1} for HNO_3 (for HNO_3 density of 1.51 g cm^{-3}), which is a maximum value. This is a substantial improvement over reported values of 620 and 54 fg g^{-1} for distilled and purified nitric acid reported by Birck et al. (1997)[6] and values of 22.5 and 30.5 fg g^{-1} reported by Mahdaoui et al. (2013; total analytical Os blanks of 170 and 230 femtogram for 5 mL of nitric acid).[22] Additionally, as shown in Figure 4, the reaction time of the first bubbling step is a useful proxy to estimate total procedural Os blank level before the actual blank values are measured; this is useful in practice for estimating whether the nitric acid is sufficiently clean for the samples under consideration. Total Os blank values less than 100 femtograms, obtained for reactions lasting over 60 min, ensure successful application of Re−Os system to geological samples with low ppb to ppt Os contents.

The isotopic compositions ($^{187}Os/^{188}Os$) of total procedural Os blanks are not correlated with nitric acid pretreatment procedures (Figure 5). Ratios of $^{187}Os/^{188}Os$ range from 0.18 to 0.89, with most ratios falling in a narrow range between 0.18 and 0.36, which is consistent with previously measured total procedural Os blanks from the AIRIE Program.[23] The scatter in $^{187}Os/^{188}Os$ ratios is likely due to the challenges of measuring such vanishingly small level of femtogram Os. These challenges

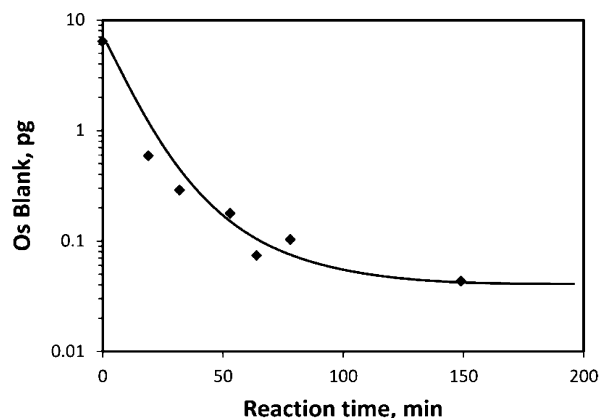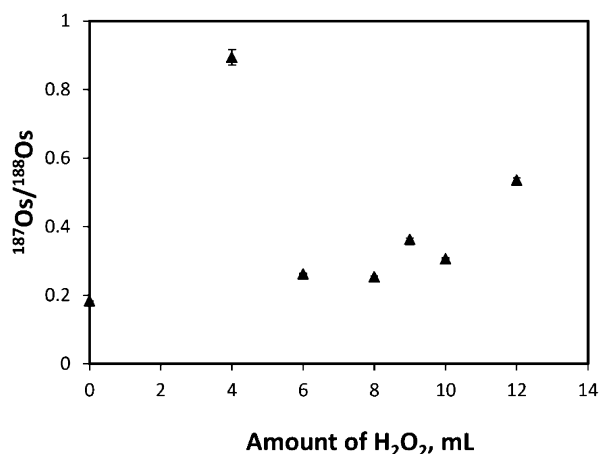**Figure 4.** Total procedural Os blank versus reaction time. Error bars are smaller than symbol size.

Figure 5. Amount of added H_2O_2 versus $^{187}Os/^{188}Os$ ratio of Os blank.

are inherent in working with blanks and include unfavorably high spike/sample ratios with large spike correction on data reduction, weak signals of 10 and 40 counts per second for ^{187}Os and ^{188}Os, respectively, and sensitivity to even the minutest amount of environmental contamination.

The results for total procedural Re blanks show a large scatter between 0.56 pg and 6.50 pg Re, with no systematic dependence on H_2O_2/HNO_3 (Figure 6). The total Re blank
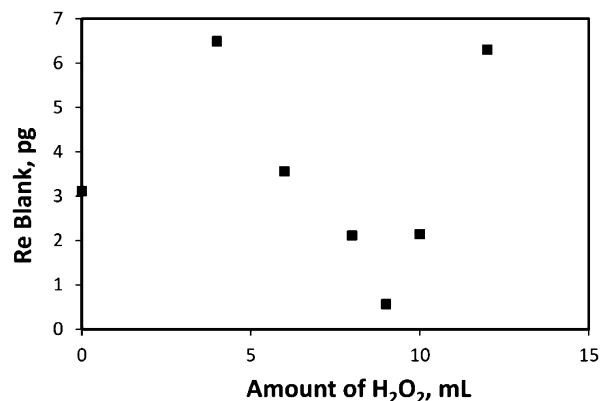

Figure 6. Amount of H_2O_2 versus total procedural Re blank. Error bars are smaller than symbol size.

obtained by untreated redistilled nitric acid is 3.12 pg, which is close to the average value of Re blanks obtained using distilled nitric acid purified with H_2O_2. The lack of correlation suggests that nitric acid is not the main source for Re blank; this is also supported by the fact that our lowest Re blank is 0.56 pg. The large and random range of Re blank suggests sources for Re blanks other than the nitric acid, and that the sources are external to our analytical procedures (e.g., environmental conditions).

■ CONCLUSION

The pretreatment of HNO_3 by H_2O_2 is a simple and fast method to reduce Os blanks. The treatment of HNO_3 proceeds in three steps: bubbling, eruption, and heating. The duration of the bubbling step is a useful proxy to estimate the Os blank in nitric acid if the baseline Os content of the nitric acid is well estimated before its use for Re−Os analysis. The amount of H_2O_2 relative to HNO_3 exerts the dominant control on Os blank reduction, whereas the use of a dry reaction beaker or the absence of fluorescent light during the bubbling step may further extend the duration of bubbling and hence reduce Os blanks. Our results suggest that optimum Os blank reduction of the nitric acid is achieved at H_2O_2/HNO_3 volume ratios of ~0.24 placed in a dry beaker and in a dark fume hood. Under these conditions, ~99% of Os in nitric acid is liberated, thereby providing a low-Os reagent for Re−Os geochronology. Our total analytical blanks include contributions mainly from the nitric acid but also from H_2O_2, HCl, HBr, and minute quantities of CrO_3. For most geological samples, however, less than 100 femtogram total procedural Os blank meets a practical necessity for successful Re−Os analysis. The significant reduction of Os blanks of nitric acid opens the door for successful applications of Os-isotopic studies and Re−Os geochronology in a variety of materials with extremely low Os contents. The Os isotopic composition of the blank is variable but mostly within the limited range of 0.18 to 0.36. This proposed pretreatment method does not reduce Re blanks; thus, conventional methods such as sub-boiling distillation are required.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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