Radiocarbon, Vol 00, Nr 00, 2024, p 1–9 DOI:10.1017/RDC.2024.36
Selected Papers from the 24th Radiocarbon and 10th Radiocarbon & Archaeology International Conferences, Zurich, Switzerland, 11–16 Sept. 2022.

IMPROVING IONPLUS MICADAS PERFORMANCE WITH RECESSED GRAPHITE

Taylor A B Broek* • Mark L Roberts

National Ocean Sciences Accelerator Mass Spectrometry Facility, Woods Hole Oceanographic Institution, 266 Woods Hole Rd., Woods Hole, MA, USA

ABSTRACT. Cathodes with recessed sample surfaces have several benefits in cesium sputter ion sources, including higher output, more efficient use of sample material, and improved focusing of the extracted ion beam. However, the Ionplus MICADAS uses cathodes with a graphite surface that is essentially flush with the sample holder. To evaluate the performance of recessed graphite with the MICADAS and determine the optimal surface depth, we tested four different depths, including the standard (flush) pressing method, 0.5 mm, 1.0 mm, and 1.5 mm. We found that recessed depths of 1.0 and 1.5 mm resulted in 20% higher ion beam current compared to the standard method under the same source conditions. The results are consistent with the beam produced from the recessed targets being more narrowly focused with a lower emittance, resulting in better transmission through the accelerator. Small graphite samples (200 μg C) with recessed surfaces produced higher currents for longer, leading to a 2–3× increase in sample ionization efficiency. Additionally, there was some evidence that isotopic ratio measurements of recessed samples were more stable over time. Overall, samples recessed to 1 mm depth offered numerous advantages over the standard pressing method and we have subsequently started pressing all MICADAS graphite using this approach.

KEYWORDS: AMS, radiocarbon, MICADAS.

INTRODUCTION

It is commonly understood within the accelerator mass spectrometry (AMS) community that the performance of some cesium sputter ion sources can be improved by recessing sample material within the target cathode. The potential benefits include higher source output, more efficient use of sample, and better focusing of the extracted ion beam. These benefits have been expressed theoretically (Middleton 1989; Vogel 2021), in models (Tiessen et al. 2021), and quantitatively (Yokoyama et al. 2010; Hlavenka et al. 2017), and recessed targets have been utilized in both commercially available and independently developed cesium sputter ion sources (e.g., NEC SNICS; Roberts et al. 2010; Broek et al. 2021, LLNL high-intensity ion source; Southon and Roberts 2000).

Despite the numerous advantages, there are limited quantitative experiments demonstrating the benefits of recessed graphite in the published literature, and no demonstrations specific to the Ionplus Mini Carbon Dating System (MICADAS; Synal et al. 2007). The potential for a better focused beam and cleaner transport would prove especially beneficial for the Ionplus MICADAS as the source output must be limited to produce high precision data. For example, using the essentially flush surfaced standard Ionplus cathodes, we found that the maximum current for stable measurements on our system is approximately 80 μA of $^{12}C^{-}$. Above this threshold there is significant evidence of beam clipping, likely at the stripper canal, including decreases in transmission and proportional increases in $^{14}C/^{12}C$ and $^{13}C/^{12}C$ ratios, suggesting issues with transport of the higher divergence ^{12}C beam.

Here we present results from an experiment designed to validate the benefits of recessed graphite with an Ionplus MICADAS and describe our subsequent implementation, measurement parameters, and resulting performance.

*Corresponding author. Email: taylor.broek@whoi.edu

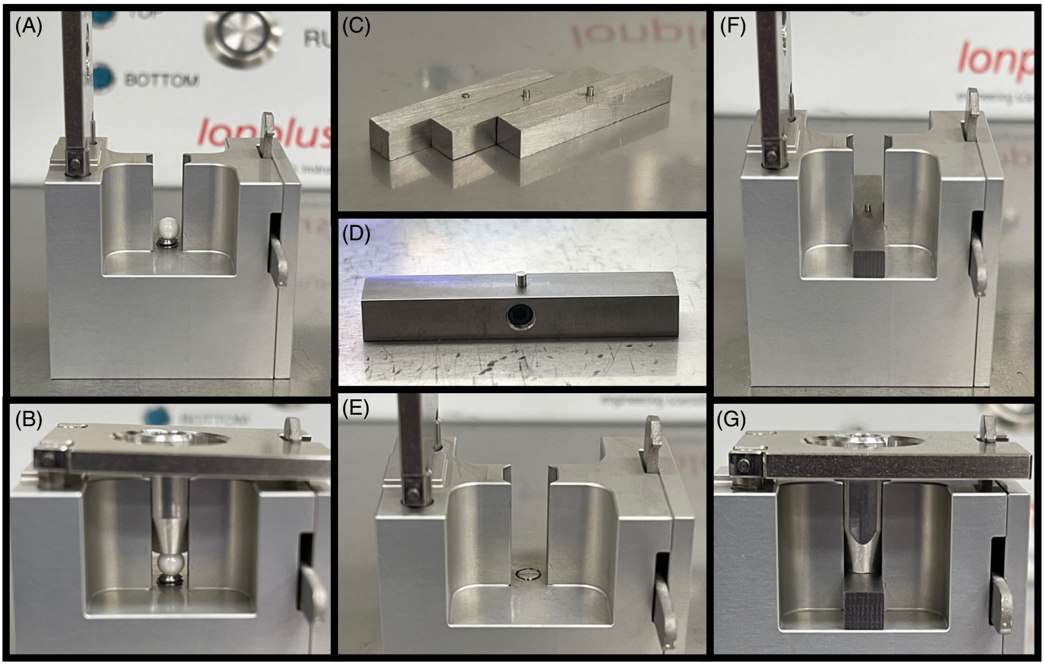

Figure 1 Target holder assembly of the Ionplus pneumatic sample press shown both without (A) and with (B) target. (C) Custom built inserts for producing targets with graphite surfaces recessed to the depths described in this study. The exposed section of the drill stems are 0.5, 1.0, and 1.5 mm in length. (D) 1 mm depth insert showing set screw for holding drill stem. (E-G) Modified target holder assembly shown with and without pressing pin and target.

MATERIALS AND METHODS

The standard solid sample targets used in the Ionplus MICADAS are rear-loaded aluminum cathodes with a 1 mm diameter sample well. The pneumatic sample pressing system (Ionplus PSP) for preparation of graphite targets includes a target holder (Figure 1A, B) that presses a 4 mm ceramic sphere against the front surface of the target and provides a clean surface for compacting the graphite, producing a graphite sputter surface that is slightly concave, with a maximum depth of less than 0.1 mm, and edges that are flush with the front of the target.

Design

In order to recess the graphite surface within the standard Ionplus targets, we produced a stainless steel insert (Figure 1C) with dimensions of 30 mm × 4.5 mm × 5.2 mm with a 1.02 mm diameter through hole and a set screw on the adjacent face. The height of the insert was matched to the height of the ceramic ball in the standard design to maintain the same tension of the spring-loaded sample holder lid (Figure 1F). This design allowed the use of 1 mm diameter drill stems cut to specific lengths to control the depth of the front graphite surface within the standard Ionplus targets. The cut end of the drill stem (pressing surface) and the top surface of the stainless steel insert were sanded to a near mirror finish to facilitate more efficient cleaning between samples and limit cross-contamination. We found that simply wiping the pin and top surface of the bar with isopropanol and a cotton swab between samples was sufficient to entirely eliminate any evidence of cross-contamination.

https://doi.org/10.1017/RDC.2024.36 Published online by Cambridge University Press

Experimental Conditions

To evaluate both the performance of recessed graphite in the MICADAS and determine an optimum surface depth, we tested 4 different graphite depths, including the standard Ionplus concave surface, 0.5 mm, 1.0 mm, and 1.5 mm. In AMS facilities that use recessed cathodes, the surface is commonly recessed to a depth approximately equivalent to the diameter of the sample well, although the optimal surface depth is likely dependent on ion source configuration. Our experimental depths were therefore chosen to bracket this expected optimal depth. For this experiment, we prepared a suite of both full-size (1 mg C) and small (200 µg C) graphite samples of modern NBS oxalic acid I (OX I; SRM-4990B) following standard NOSAMS sample preparation protocols (Gagnon et al. 2000). We pressed 3 full-size samples and 1 small sample to each depth. The full-size samples were used to evaluate ion source output and system stability, whereas the small samples were intended to evaluate ion source efficiency.

The MICADAS instrument was tuned at a cesium reservoir temperature of 120°C using a sample pressed with the standard Ionplus method and all samples were analyzed with the same source and beamline element parameters. The distance between the ionizer and sample holder was optimized for maximal efficient use of the standard flush mounted Ionplus targets, such that the focal point of the cesium beam was in front of the target surface, resulting in a ring shapped sputter pattern (e.g., Fallon et al. 2007). The samples were analyzed in "Auto Measurement" mode for 30 passes of 180 seconds (15 cycles of 12 seconds) with a 5 second stabilization time and no burn in cycles. The 30 measurement passes of each target (representing 5550 seconds of cesium exposure time) were enough to produce a significant drop in the current output from the small-sized samples to well below the initial output but not sufficient to completely consume all graphite. In contrast, the full-size samples showed no decrease in current during the measurement period.

For the experiment described herein, all physical source settings were held constant, including the physical distance between various source stages (e.g., the ionizer, immersion lens, and sample stage). We note that in order to modify the z-position of the cathode in the Ionplus MICADAS source, the source must be opened to the atmosphere, potentially resulting in undesirable variability in source performance that would be difficult to distinguish from changes due to the recessed depth of the graphite. Therefore, for this experiment, in changing the amount of recess, the distance between the graphite surface and both the ionizer and immersion lens also changed between samples, resulting in slight differences in cesium focus on each graphite surface. Future experimentation could employ modified targets which would allow for different graphite recess depths while holding constant the distance between the graphite surface, ionizer, and immersion lens.

RESULTS AND DISCUSSION

Ion Beam Current

Perhaps the most significant effect of recessed graphite was seen in C^- ion beam production (Figure 2). At the source parameters chosen for this experiment (Cs reservoir = 120°C), the standard pressing method produced an average of 70 ± 4 µA of $^{12}C^-$ beam over thirty 180 second measurements. The 0.5 mm depth recessed targets showed a modest increase, with average $^{12}C^-$ currents of 74 ± 4 µA. However, the 1.0 mm and 1.5 mm recessed targets produced significantly more current, with average values of 84 ± 5 µA and 85 ± 7 µA respectively.

https://doi.org/10.1017/RDC.2024.36 Published online by Cambridge University Press

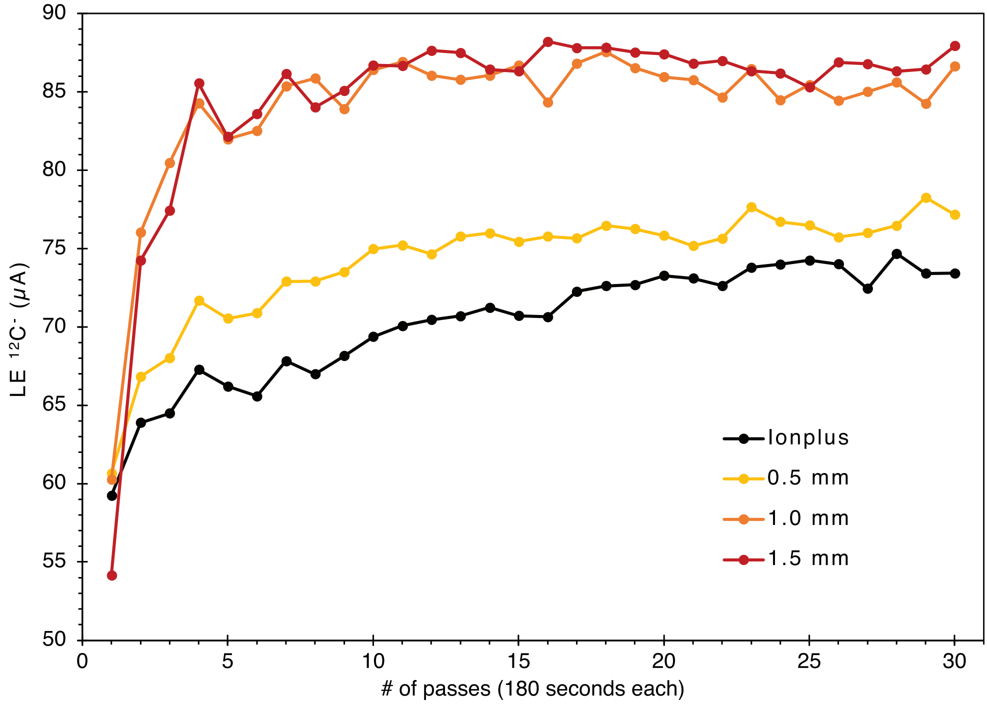

Figure 2 Current output (measured as μA of low-energy $^{12}C^{-}$) from graphite targets containing 1 mg C pressed to different depths. Each point represents the average current of n=3 separate targets measured over a 180-second pass (15 cycles of 12 seconds each).

It is possible that some of the increase in ion beam current is due to changing the distance between the ionizer and the graphite surface and coincident change in cesium beam focusing. Both the diameter of the cesium beam and the geometry of the sputter patter at the graphite surface would influence the magnitude of C^{-} production. However, we also hypothesize that the higher electron density within the enclosed sample well area leads to more efficient ionization of the sample material resulting in higher ion currents. It should be noted that the ion currents of the 1.0 and 1.5 mm recessed samples are higher than the typical 80 μA cutoff above which we typically observe beam transport and stability issues, however, these deleterious effects were not seen in these measurements (discussed in more detail below).

Efficiency

The relative duration of ion beam production from the small-sized samples can be used to evaluate differences in the ionization efficiency (i.e., conversion of C to C^{-}) between recessed sample depths. However, because the targets were not sputtered to exhaustion, a minimum current cutoff of 40 μA was chosen when calculating the efficiency of each target. I.e., when the average current output of an individual pass dropped below this cutoff it was excluded from the calculation. Using this method to calculate a relative ionization efficiency, there is a clear relationship between efficiency and recessed surface depth (Figure 3). The target pressed with the standard method produced a C^{-} beam > 40 μA for a total of 9 passes (~1665 seconds of sputtering) during which approximately 6.1% of the sample C was ionized and extracted. There was a small increase in efficiency at 0.5 mm

https://doi.org/10.1017/RDC.2024.36 Published online by Cambridge University Press

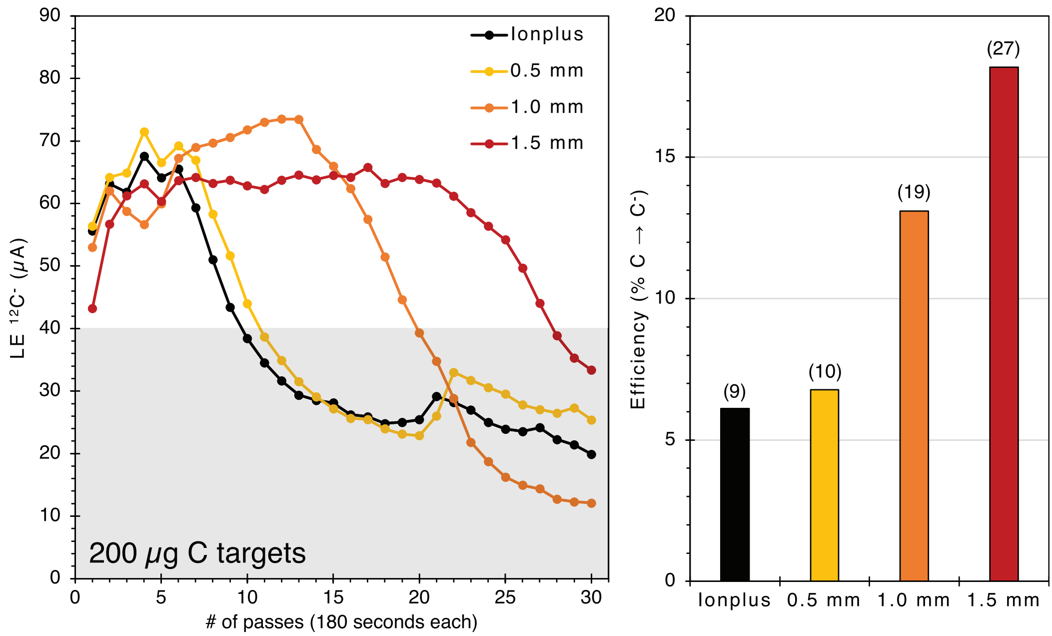

Figure 3 Left panel: current output (measured as μA of low-energy $^{12}C^-$) from graphite targets containing 200 μg C pressed to different depths. Each point represents the average current of a single target measured over a 180-second pass (15 cycles of 12 seconds each). Shaded region represents measurements excluded from the efficiency calculation. Right panel: summed total conversion of C to C^- of each target during measurement passes where the average $^{12}C^-$ current was greater than 40 μA. The number in parentheses above each bar denotes the number of passes with an average current above 40 μA that were used in efficiency calculations.

depth, with the target lasting for 10 passes (~1850 seconds) resulting in 6.8% of the sample measured as C^-. The most significant efficiency gains were observed in the 1.0 and 1.5 mm recessed samples, which maintained C^- current > 40 μA for 19 and 27 passes respectively (~3515 and 4995 seconds), representing 13.1 % and 18.2 % conversion of C to C^-. It should be noted that the accelerator transmission is ≤ 50% and therefore the C to C^+ efficiency is approximately one-half the value shown for C to C^- conversion.

This 2- to 3-fold increase in ionization efficiency in the deeper recessed samples can be partially explained by the same factors that lead to higher beam currents in recessed full-size samples discussed above. However, the absolute differences in maximum ion current between small samples at different depths were modest and the extended duration of high-current production from recessed targets was a more significant factor in increasing the calculated efficiency. Changes in the cesium focus and resulting differences in the geometry of the cesium sputter pattern likely influence the duration of high current production from small samples. Therefore, it is possible that the cesium focus at the surface of the 1.0 and 1.5 mm recessed samples was better optimized for more efficient utilization of the graphite. However, we also hypothesize that the increased surface area within the deeper recessed targets acts as a surface to which sputtered neutral C can be redeposited and remain available for subsequent re-sputtering and ionization.

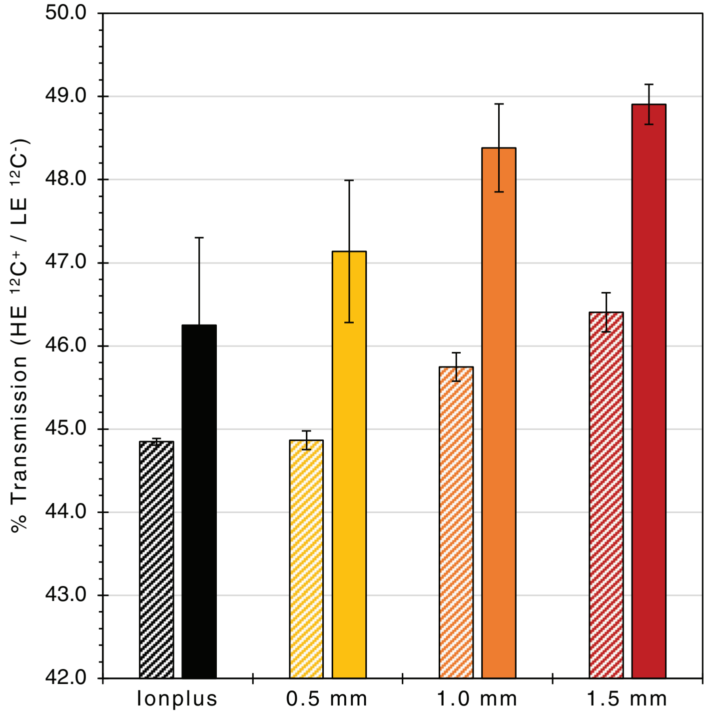

Figure 4 Transmission (measured as the ratio of high-energy $^{12}C^{+}$ to low-energy $^{12}C^{-}$) from graphite targets containing 200 μg C and 1 mg C pressed to different depths. Each bar represents the average transmission of n=3 1 mg C targets (dashed bars) or a single 200 μg C target (solid bars) measured over thirty 180-second passes (15 cycles of 12 seconds each).

Transmission

There was a positive relationship between the recessed sample depth and the transmission through the tandem accelerator (measured as the ratio of high-energy $^{12}C^{+}$ to low-energy $^{12}C^{-}$), with significantly higher transmission in more deeply recessed targets (Figure 4). The full-sized standard Ionplus targets and 0.5 mm recessed targets had indistinguishable average transmission values of 44.8 ± 0.1% and 44.9 ± 0.1% respectively. The 1.0 mm targets had an average transmission of 45.7 ± 0.2% and the 1.5 mm targets = 46.4 ± 0.2%. We hypothesize that the increased transmission from recessed samples compared to flush samples is primarily the result of a lower beam emittance due to confinement of the C^{-} beam exiting the recessed target and subsequent cleaner transport through the accelerator. It is also possible that the narrower, lower-emittance beam is more efficiently stripped in the stripper canal, resulting in more $^{12}C^{+}$ ions reaching the HE offset Faraday cup. The relationship between recessed depth and transmission was seen in both the full size and small samples; however, the transmission was significantly higher for the 200 μg samples than the full-sized samples in all cases (standard Ionplus = 46.3 ± 1.1%, 0.5 mm = 47.1 ± 0.9%, 1.0 mm = 48.4 ± 0.5%, 1.5 mm = 48.9 ± 0.2%). In fact, the highest average transmission seen in the full-sized samples was equivalent to the lowest average transmission seen in the small-sized samples. This clear difference in transmission between the full-size and small samples provides additional support for the

https://doi.org/10.1017/RDC.2024.36 Published online by Cambridge University Press

emittance hypothesis because it demonstrates that differences in the relative emittance of the ion beam can influence transmission in this system.

An alternate explanation for the differences in transmission could be that the higher current, higher emittance ion beam from the 1.0 and 1.5 mm recessed targets lead to some $^{12}C^{-}$ beam being excluded from measurement in the low-energy offset faraday cup and artificially increasing the high-energy $^{12}C^{+}$ to low-energy $^{12}C^{-}$ ratio. However, this is not consistent with what is typically seen with high current ion beams in this system, namely a *decrease* in transmission and preferential loss of high-energy $^{12}C^{+}$ above the 80 μA $^{12}C^{-}$ cutoff described previously.

Stability

An unexpected result of this experiment was the emergence of an apparent relationship between the target recess depth and the stability of isotopic ratios over the course of the analysis (supplemental Figure 1). This effect was seen most dramatically in the raw $^{14}C/^{12}C$ ratios, where the standard pressed sample and the 1.5 mm depth recessed samples both drifted by >2% over the 30 passes, although in opposite directions (standard method target drifted down, 1.5 mm target drifted up). This drift was more than double the magnitude of the offset between the highest and lowest ratios measured for the 0.5 and 1.0 mm targets. However, this ultimately did not affect the calculated fraction modern of the measurements because a proportional drift was also seen in the $^{13}C/^{12}C$ ratio and therefore any drift was negated by the ^{13}C correction.

It is unclear what produced these trends, however, with the exception of the 1.5 mm recessed targets, the areas of the experiment with the greatest drift in raw ratios appeared to coincide with the largest changes in ion current. This potentially suggests that the drift is related to the current dependence on isotopic ratios which is known to be present with MICADAS. If so, the limited drift in the targets recessed to 0.5 and 1.0 mm might suggest that the current dependence or isotopic fractionation in the source is at least partially ameliorated by recessing the graphite. The limited drift, or increase stability, in the 0.5 and 1.0 mm targets can also potentially be explained by the lower emittance beam having more running room, such that fluctuations in the source throughout the run have less effect on the high energy C^{+} beam.

CONCLUSIONS

Samples pressed with recessed surfaces performed significantly differently than samples prepared with the standard Ionplus pressing method, resulting in several tangible improvements to MICADAS system performance. By recessing the graphite surface alone, we were able to increase the current output from the ion source by approximately 20%. The ion current increase was accompanied by an increase in transmission through the accelerator, consistent with a better focused, lower emittance beam, and leading to the elimination, or at least significant increase, of the previous 80 μA C^{-} beam current limitation for high-precision measurements. These combined effects permit the detection of more ^{14}C atoms per unit time, either reducing the necessary measurement time or increasing the attainable precision within a set measurement time. Another significant effect of recessing samples was a major increase in the ionization efficiency of small graphite samples. The greater than 2-fold increase in ionization efficiency has important implications for the attainable precision when measuring small graphite samples. In addition, although less obvious and harder to explain than the other improvements, there appears to be some impact from recessed targets on the overall stability of isotopic ratio measurements. If our hypothesis is correct that this trend suggests a minimization of the current dependence of the system, recessed graphite could potentially expand our ability to measure graphite samples over a larger range of sample sizes.

We note that due to the specific design of the experiment described herein, it is likely that some of the observed effects resulted from changes in the cesium beam focus and geometry of the sputter pattern at the graphite surface rather than the specific recessed depth of the graphite surface alone. That is to say, it is possible that by recessing the graphite surface, we achieved a more optimal spacing between the graphite surface and the ionizer. However, the observation of concurrent increases in both ion beam current and sample use efficiency provide some evidence that this is not the only effect being observed. Specifically, in other systems, the cesium focus which produces the highest ion beam currents is typically not the same as that which results in the most efficient use of the graphite target (Fallon et al. 2007). Therefore, it is likely that the recessing of the graphite surface is responsible for a number of the performance improvements seen here. Future experiments should be conducted to isolate the influence of cesium focus from that of recessed graphite depth. This could be accomplished through the use of modified targets which allow the graphite to be recessed while maintaining an equal distance between the ionizer and graphite surface.

Since the initial recessed depth comparison experiment described above, we have begun recessing all graphite targets to 1 mm depth. In order to compensate for the difference in distance from the ionizer to the graphite surface between standard pressed and recessed targets we adjusted the z-position of the target by decreasing the distance between the ionizer stage and target stage by approximately 0.5 mm. This move further optimized the cesium focus at the graphite surface and provided an additional increase in ion current. With the source positioned and tuned specifically for the recessed target, we now routinely produce a C^- beam between 90 and 110 μA (average = 99.2 ± 2.4 μA, n=30) at a cesium temperature of 120°C (compared to 80.3 ± 6.9 μA, n=22 for non-recessed targets), with no decrease in transmission or evidence of diminished stability. Further, a more carful tune of beamline elements specific to full size recessed graphite samples improved transmission through the accelerator to 48.9 ± 0.3 % (n=30).

ACKNOWLEDGMENTS

The authors would like to thank the NOSAMS Sample Preparation Laboratory for preparing graphite samples for this study and Brett E. Longworth for help with data processing and analysis. This work was supported by a cooperative agreement with the U.S. National Science Foundation (NSF-OCE-17551).

SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit https://doi.org/10.1017/RDC.2024.36

REFERENCES

Broek TAB, Ognibene TO, McFarlane KJ, Moreland KC, Brown TA, Bench G. 2021. Conversion of the LLNL CAMS 1 MV biological AMS system to a semi-automated natural abundance ^{14}C spectrometer: system optimization and performance evaluation. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 499:124–132.

Fallon SJ, Guilderson TP, Brown TA. 2007. CAMS/LLNL ion source efficiency revisited. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 259:106–110.

Gagnon AR, McNichol AP, Donoghue JC, Stuart DR, von Reden K. 2000. The NOSAMS sample preparation laboratory in the next millennium: Progress after the WOCE program. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 172:409–415.

Hlavenka JD, Abrams H, Roberts ML, Longworth BE. 2017. Increased AMS ion source efficiency and ion currents by modifying SNICS cathode material and geometry. Physics Procedia 90:17–21.

Middleton R. 1989. A negative ion cookbook [unpublished]. University of Pennsylvania.

Roberts ML, Burton JR, Elder KL, Longworth BE, McIntyre CP, von Reden KF, Han BX, Rosenheim BE, Jenkins WJ, Galutschek E, McNichol AP. 2010. A high-performance ^{14}C accelerator mass spectrometry system. Radiocarbon 52:228–235.

Southon J, Roberts ML. 2000. Ten Years of Sourcery at CAMS/LLNL- Evolution of a Cs Ion Source. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 172:257–261.

Synal HA, Stocker M, Suter M. 2007. MICADAS: A new compact radiocarbon AMS system. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 259:7–13.

Tiessen C, Kieser W, Zhao X. 2021. Optimizing a cesium-sputter ion source using Lorentz 2E. 15th Conference on Accelerator Mass Spectrometry (AMS-15). Sydney, Australia.

Vogel J. 2021. Potential ways to increase C^- from CO_2-fed sputter sources. 15th Conference on Accelerator Mass Spectrometry (AMS-15). Sydney, Australia.

Yokoyama Y, Koizumi M, Matsuzaki H, Miyairi Y, Ohkouchi N. 2010. Developing ultra small-scale radiocarbon sample measurement at the University of Tokyo. Proceedings of the 20th International Radiocarbon Conference. Radiocarbon 52:310–318.

https://doi.org/10.1017/RDC.2024.36 Published online by Cambridge University Press