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A NOTE: RADIOCARBON DATA COMPARISON OF SMALL GASEOUS SAMPLES MEASURED BY TWO MICADAS AT ETH ZURICH AND OCEAN UNIVERSITY OF CHINA

M Chu[1,2] • R Bao[1,2,3]*

[1]Frontiers Science Center for Deep Ocean Multispheres and Earth System, Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, and Center for Ocean Carbon Neutrality, Ocean University of China, Qingdao, China

[2]Laboratory for Marine Ecology and Environmental Science, Qingdao National Laboratory for Marine Science and Technology, Qingdao, China

[3]Department of Earth Sciences, Geological Institute, ETH Zurich, Zurich, Switzerland

ABSTRACT. A MIni CArbon DAting System (MICADAS) has been recently installed at the Ocean University of China (OUC) mainly for determining the radiocarbon (^{14}C) ages for marine sedimentary organic carbon. In this study, we compared the data from a series of CO_2 samples measured independently by the MICADAS at OUC and ETH Zurich to assess whether the data from the OUC MICADAS meet our requirement for carbon cycle research. The measured samples covered a range of ^{14}C ages from 1229 to 12,287 yr, and size from 5 to 162 µg C. The data from the two instruments showed a good linear relationship with only small ^{14}C age offsets, meeting our research demands such as carbon source apportionment. Lastly, we propose that for MICADAS clients, such a cross-lab comparison of the size- and age-dependency of MICADAS using age-known samples is important for ^{14}C data integration.

KEYWORDS: inter-comparison, MICADAS, Ocean University of China, radiocarbon, small gaseous samples.

INTRODUCTION

Radiocarbon (^{14}C) dating technology has been applied widely in organic geochemical studies. In particular, carbon cycle related investigations (e.g., compound-specific radiocarbon analysis) often require quick measurements of small-sized samples to get adequate information from samples with limited sizes. To provide quick ^{14}C measurements for small-sized CO_2 gaseous samples (Fahrni et al. 2013; Haghipour et al. 2019; Molnár et al. 2021), the MIni CArbon DAting System (MICADAS) was developed at ETH Zurich (Synal et al. 2007). MICADAS has now been commercialized and set up among research institutions (e.g., Schulze-König et al. 2010; Bard et al. 2015), in applications including carbon cycle studies (Eglinton et al. 2021), paleoclimate reconstruction (Gottschalk et al. 2018), archeological dating (Cersoy et al. 2017) and biomedical research (Schulze-König et al. 2010).

Carbon cycle researchers often assign samples of various types (sedimentary organic carbon, carbonates, etc.) to be measured by different laboratories. The reproducibility of ^{14}C measurements varies among institutions (Quarta et al. 2021), which emphasizes the importance of cross-comparison of the data obtained from different platforms. In addition, the growing needs of international collaboration of the science community should also be supported by a comparison between different MICADAS platforms. To address these needs, measurement of small-sized (<50 µg C) split gaseous samples by different MICADAS is especially informative, as (a) the performance of the MICADAS is conventionally calibrated by a series of mg-sized standard samples (i.e., NIST Oxalic Acid, higher fraction modern [Fm]) that may not always fit the demand of real sample measurements (e.g., limited sizes, low Fm), and (b) the direct comparison by gaseous samples excludes the influences from original sample types and the preparation methods used at different MICADAS platforms. Therefore, for MICADAS clients whose research requires relatively low ^{14}C measurement precision (e.g., carbon source apportionment),

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*Corresponding author. Email: baorui@ouc.edu.cn

measuring split gaseous samples by different instruments helps to verify whether the data can meet the research demands with acceptable cross-platform offsets.

A MICADAS was installed in 2019 at the Radiocarbon Accelerator Mass Spectrometry Laboratory at the Ocean University of China (OUC-CAMS) and is providing services for users. For clients, any cross-platform ^{14}C measurement offsets could possibly lead to misleading interpretations. A practical and effective assessment of the data consistency between MICADAS platforms is therefore crucial to guarantee data integration and interpretation. This article addresses this need by measuring a series of CO_2 samples that cover a ^{14}C age range from approximately 1000 to 12,000 yr, as well as a size range of 5 to 162 μg C, using the MICADAS at OUC. The split gaseous samples have been previously measured by MICADAS at the Laboratory of Ion Beam Physics at ETH Zurich. Our focus is to examine whether the ^{14}C data measured by the newly established MICADAS at OUC can be integrated with the data obtained from other platforms. Through a cross-platform ^{14}C data comparison, we present an example to quickly assess and understand the data quality from a newly established infrastructure.

METHOD

The gaseous samples were prepared from marine sediments, combusted via a sealed tube method, split into μg-sized portions on vacuum line and measured at ETH Zurich (Bao et al. 2018a, 2018b). The residual samples were again split on vacuum line at OUC before measured at OUC. To test the age-dependency of ^{14}C measurement at OUC, a series of samples with an age gradient were split into similar sizes (29–51 μg C, Table 1). In addition, to test the potential mass-dependent performance, one sample with an ^{14}C age of approximately 2.6 kyr was split into five portions with different masses at OUC (Table 1). The 0.2MV MICADAS at OUC employs helium stripping, which gives a transmission efficiency of about 50%. Its main feature is the inclusion of a gas interface system (GIS). The ion source can accept CO_2 gas introduced through a capillary fitted to the GIS into specially designed targets (Wacker et al. 2013). Sample CO_2 is mixed with helium and the mixture is continuously fed into the ion source by means of a gas syringe driven by a stepping motor. Before the CO_2 sample measurements, the MICADAS system had undergone data quality validation using IAEA standards. The measured values were subjected to quality control and were in good agreement with their reference values (personal communication with technician at OUC-CAMS).

RESULTS AND DISCUSSION

Four gaseous samples were measured independently at OUC and ETH Zurich (Table 1 and Figure 1a). The average ^{14}C age offsets of samples A–D measured by the two MICADAS is 86 yr. The measured age differences of samples A, B, and D lie within $\pm 2\sigma$ of OUC measurement (Table 1). In our view, this is an acceptable precision for small-sized gaseous sample measurement for a newly established MICADAS. The absolute ^{14}C age differences between OUC and ETH Zurich are at the same order of magnitude (148 yr for the youngest sample, and 123 yr for the oldest sample, Table 1), showing a tendency toward higher data consistency between the two platforms with increasing sample ages.

Portions of one sample were introduced into the MICADAS at OUC with different sample masses (Table 1 and Figure 1b). All age differences between the two platform are within $\pm 1.5\sigma$ of the OUC measurement, while OUC measurement has overall higher uncertainties

Table 1 Information of the split gaseous samples. The uncertainties were errors from an individual measurement.

	ETH Zurich measurement*			OUC measurement			^{14}C yr offset
Sample label	Lab code (ETH-)	Mass (µg C)	Conventional age (^{14}C yr)	Lab code (OUC-)	Mass (µg C)	Conventional age (^{14}C yr)	ETH–OUC (^{14}C yr)
A	62410	101	1377 ± 80	1216.1.6	29	1229 ± 101	148
B	62626	94	2472 ± 96	1216.1.7	45	2404 ± 98	68
C	62395	108	5501 ± 87	1216.1.8	51	5249 ± 115	252
D	62391	24	12,164 ± 145	1216.1.9	48	12,287 ± 175	−123
E-1	65127	130	2640 ± 102	1216.1.1	162	2504 ± 95	136
E-2				1216.1.2	88	2551 ± 90	89
E-3				1216.1.3	15	2531 ± 130	109
E-4				1216.1.4	8	2350 ± 226	290
E-5				1216.1.5	5	2277 ± 419	363

*Data of ETH Zurich measurement was first reported in Bao et al. (2018a, 2018b).

than ETH Zurich (Table 1). The average ages show a tendency towards younger ages in smaller-sized samples (Figure 1b). Ruff et al. (2010a, 2010b) reported a higher influence of constant contamination for samples < 8 µg C at the MICADAS of ETH Zurich. Meanwhile, the measurement of IAEA standards that contained > 15 µg C had higher precision and agreed with their consensus values (Figure 1b). Similarly, while the measured ^{14}C ages increase with sample sizes at OUC, they become constant among bigger-sized samples (E-1 and E-2), consistent with the performance of the MICADAS at ETH Zurich (Figure 1b). Our results agree with former reports that counting statistics (Gottschalk et al. 2018) and/or contamination (Mollenhauer et al. 2005) exert larger influence on smaller-sized samples. The current at high-energy side of the MICADAS was below 3 µA when measuring samples that are < 10 µg C at OUC, suggesting that this size dependency is partly caused by the secondary ions produced from samples (Salehpour et al. 2016). Similarly, the ion current increased within the sample sizes of 20 µg C and stabilized for samples when containing > 20 µg C in a case of MICADAS at Aix-Marseille University (Tuna et al. 2018). For the same reason, gaseous samples were recommended to contain 10–30 µg C for paleoenvironmental research at Curt-Engelhorn-Centre for Archaeometry and the University of Bern (Gottschalk et al. 2018; Lindauer et al. 2019). Contamination may be introduced during sample handling (Tuna et al. 2018) and AMS measurement (Mollenhauer et al. 2005). These additional CO_2 sources may also cause greater impact on smaller-sized (and older) samples with higher uncertainties (Gottschalk et al. 2018), which can be partly eliminated by data extrapolation and calibration (e.g., Aerts-Bijma et al. 2021). Overall, our results agree with Ruff et al. (2010a, 2010b) that a lower limit of 10~15 µg C is recommended in order to guarantee the best performance of the MICADAS at OUC.

The overall precision and reproducibility of the MICADAS at OUC are acceptable for our organic geochemical investigations, although further evaluation is needed for dating purposes. It is important for clients to quickly assess the data reliability and comparability of a newly-established infrastructure (MICADAS, AMS, etc.) in order to interpret multi-sourced ^{14}C data. A practical note from the perspective of MICADAS clients is therefore

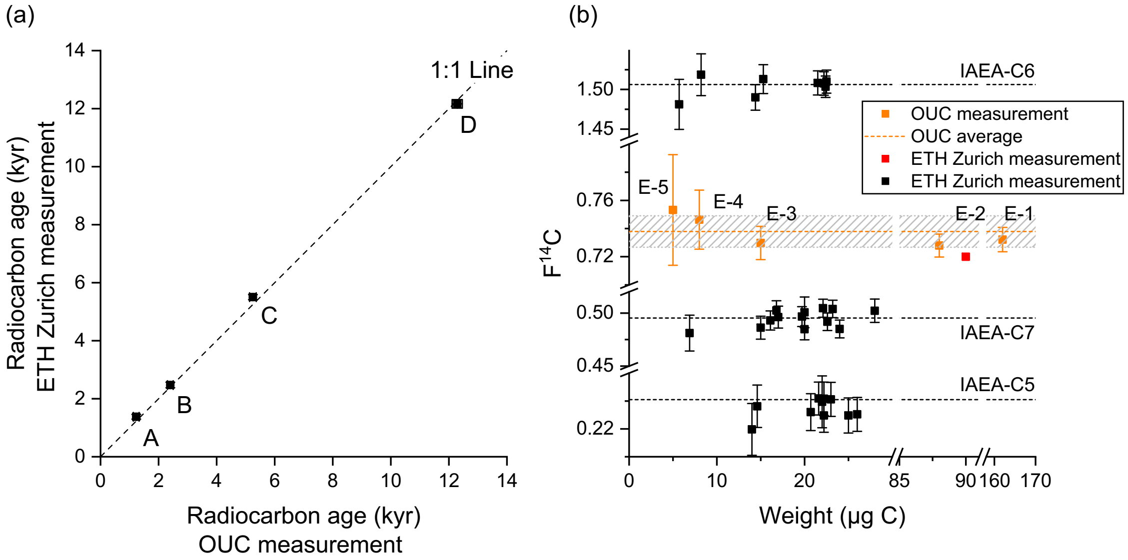

Figure 1 (a) Comparison of ^{14}C results at ETH Zurich and OUC. (b) ^{14}C measurement as a function of sample size. The orange symbols are measured ^{14}C ages of sample E, with average value (dotted line) and standard deviation (shaded area). The red symbol is the ^{14}C ages measured at ETH Zurich. The black symbols represent measurements of IAEA standards at ETH Zurich (Ruff et al. 2010a, 2010b). (Please see online version for color figure.)

informative, although a systematic evaluation is needed from OUC-CAMS in the future. Measurement precision of MICADAS is both size- and age-dependent (Bard et al. 2015; Gottschalk et al. 2018), and this dependency further varies among institutions (Quarta et al. 2021), which can be better clarified by measuring age-known samples as a practical inter-lab secondary standard. We propose a quick comparison of the size- and age-dependent performance of MICADAS using age-known gaseous samples between laboratories that are currently equipped with MICADAS, which will provide a context for carbon cycle researchers to assess the cross-lab ^{14}C data comparability.

CONCLUSION

An evaluation of the MICADAS at OUC is carried out by measuring a set of split gaseous sample sized from 5 to 162 µg C, as well as a series of gaseous samples aged from 1229 to 12,287 ^{14}C yr. The results are then compared with those obtained from ETH Zurich. The results from the two platforms are in good linear relationship, with a recommended lowest sample size of 15 µg C to avoid large uncertainties at OUC. Our results demonstrate that by measuring split gaseous samples, an economical and efficient assessment of ^{14}C data comparability and offsets between infrastructures could be conducted for clients, providing a basis for cross-platform ^{14}C data integration. With more AMS being set up, we motivate more global cross-platform comparisons of ^{14}C measurements using split gaseous samples as intra -laboratory secondary standards, which will aid in cross-platform collaboration and scientific interpretation of ^{14}C data.

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