Standard operation procedures and performance of the MICADAS radiocarbon laboratory at Alfred Wegener Institute (AWI), Germany

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ABSTRACT

The radiocarbon analysis laboratory at Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research (AWI) is equipped with an accelerator mass spectrometer (AMS) MICADAS (MIni CArbon Dating System). The laboratory provides routine ^{14}C analyses on bulk organic matter, plant fragments, dissolved and particulate organic matter, individual molecular lipids, and carbonate (micro-) fossils with the aim to foster international research efforts in vulnerable high latitudes. The AWI MICADAS allows AMS ^{14}C analysis on graphite targets as well as on CO_2 samples via gas injection into the hybrid ion source. The laboratory thus provides reliable datasets even if only small amounts of sample material are available, a problem often encountered in polar research. Here we describe the standard operation procedures and sample preparation methods employed, and demonstrate the instrument performance and data quality based on repeat analysis of international reference materials.

1. Introduction

At the end of 2016, a new laboratory for radiocarbon analyses of samples used for polar and marine research was established at Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research in Bremerhaven, Germany. It is equipped with an accelerator mass spectrometer (AMS) MICADAS (MIni CArbon DAting System) from Ionplus, a compact AMS developed by ETH Zürich [1,2] with a hybrid ion source allowing sample introduction as CO_2 gas or graphite [3,4]. The ion source is connected to a versatile gas interface system [3]. The capability of analyzing gas samples allows the focus on samples of marine carbonate fossils, small plant remains, and specific organic compounds, as these types of materials extracted from samples from the polar regions are typically small (<500 µgC).

At AWI MICADAS, routine analyses are performed on samples of total organic matter in natural marine sediments [5,6] and terrestrial deposits [7], of plant fragments [8,9], of particulate organic carbon (POC) sampled on glass-fiber filters, of dissolved organic carbon (DOC) from lakes and rivers, of purified organic compounds [10], and of carbonate samples from marine (micro-)fossils [11–13].

Here we describe the standard methodology used for routine sample preparation and review the performance of the facility based on analyses

of certified standard materials and repeat measurements of laboratory internal standards.

2. Instrumentation

2.1. Accelerator mass spectrometer

The MICADAS at AWI (Fig. 1) is specifically designed and dedicated to perform radiocarbon analyses and is based on a design described elsewhere [1,2,14]. The samples are introduced into the vacuum of the instrument via a linear magazine holding up to 39 gas or graphite cathodes. The main advantage of the instrument is the hybrid cesium sputter ion source, which generates negative carbon ions from the sample which are accelerated by a −38 kV potential [2]. The tandem accelerator of up to 200 kV is provided by a solid-state power supply, and the terminal is vacuum insulated (no SF_6 or other insulation gases required). At AWI it operates at 185.25 kV using helium of ultra-high purity (99.9999%) instead of nitrogen as stripper gas, which results in an overall transmission of about 47% for carbon ions. To separate the ions after double stage acceleration, MICADAS is operated on the high energy end with a 90° dipole permanent magnet with sigmatic beam forcing properties. $^{12}C^+$ as well as $^{13}C^+$ ions are detected by Faraday

cups. $^{14}C^+$ ions enter an energy filter (electrostatic analyzer, ESA) before hitting a silicon nitride window which is part of the gas ionization detector. This gas ionization chamber filled with isobutane includes low noise integrated preamplifiers.

Data acquired during measurement are processed using the BATS (v. 4.30) software, including automated corrections for blank, isotope fractionation, and systematic effects (e.g., time shift correction), data normalization and uncertainty calculations (see [15] for full details).

2.2. Graphitization unit

An automated graphitization system (AGE-3; Ionplus AG; [16]) allows fast and fully-automated graphitization of up to 7 samples per run. Depending on the type of samples the AGE-3 is coupled to an elemental analyzer (Elementar vario Isotope) for organic matter samples, or the carbonate handling system (CHS, Ionplus AG; [4]) for carbonates, to prepare graphite samples (0.4 – 1 mgC). CO_2 from any preparation unit is carried by a stream of helium to an adsorption trap (13X zeolite). CO_2 is trapped by adsorption on the trap at room temperature. After this preconcentration of CO_2 and evacuation of the trap to remove the carrier gas, the trap is heated to 420 °C for 50 s and kept at this temperature for 10 s. CO_2 desorbs from the zeolite and is transferred to the evacuated graphitization reactor by gas expansion, and hydrogen gas is added as reactant. Iron powder (SIGMA ALDRICH; CAS:7439–89-6) is used as a catalyst with about 4.2 mg of Fe for 1 mgC. The reactors are heated by an oven to 580 °C for 120 min, and water is removed in traps cooled by Peltier elements.

2.3. Graphite sample processing

The graphite samples are pressed into cathodes using a pneumatic press; cathodes are inserted into the linear magazine holding up to 39 samples. A magazine contains up to 23 unknown samples, 4 secondary standards and 6 normalization standards (NIST Oxalic Acid II (OxAII); NIST SRM4990C) and 6 blanks (Phtalic Acid (PhA); Sigma Aldrich 320064, Lot # MKBZ4209V; Table 2), which are matched in size to, and processed in the same way as, the unknown samples (see below). Each graphite target is analyzed typically in 8 runs of 6 min to obtain about 3 × 10^5 counts of $^{14}C^+$ ions for the OxAII standard resulting in a mean analytical precision derived from counting statistics of ± 1.9‰.

2.4. Gas sample processing

Beside conventional solid graphite samples the ion source also accepts CO_2 gas introduced through a capillary fitted to the Gas Interface System (GIS, [3]) into specially designed gas cathodes [2]. The GIS produces a gas mixture of CO_2 and He, which is introduced continuously under constant pressure and flow into the ion source. The GIS can handle CO_2 gas originating from various peripheral systems. It can introduce CO_2 from (i) gas bottles containing normalization standards and blanks; (ii) from the automated glass tube cracker; (iii) the carbonate handling system (CHS); or (iv) the elemental analyzer (EA). Normalization standards and blanks are produced from Oxalic acid II and blank (PhA) combusted to CO_2 and mixed with He (5% CO_2). CO_2 produced by the peripheral systems is first concentrated on the zeolite trap contained within the GIS and then released by heating of the trap to 450 °C and transferred by gas expansion into the injection syringe. Here the gas is manometrically quantified and He is added to obtain a gas mixture of ~ 5% CO_2 in He. The gas mixture is subsequently fed to the ion source. To minimize cross contamination the zeolite trap is baked off at 450 °C for 2 min and constantly flushed with He. After the cleaning process, the trap is cooled down to room temperature. Gas samples are typically analyzed for 12 min at a constant feeding rate of 2.4 μgC min^{-1}, that results in a stable $^{12}C^+$- beam between 5 and 8 μA and about 3 × 10^4 counts of $^{14}C^+$ ions for the Oxalic Acid II gas standard (OxAII gas; Ionplus) resulting in a mean analytical precision derived from counting statistics of ± 5.8‰.

3. Sample preparation and analytical procedures

3.1. Organic matter combustion by Elemental Analyzer

3.1.1. Sediment total organic matter
Samples of sediment are weighed using forceps and scoops cleaned in 99.9% 2-propanol into silver boats (Table 1) and decarbonated by the addition of three drops of 6 M distilled hydrochloric acid (HCl), covered and allowed to dry on a 60 °C hot plate. The decarbonation and drying process is repeated twice more, for a total of 3 acid additions. In this way, we ensure that the fine fraction is not washed away. If a sediment sample has a very high inorganic carbon content, the decarbonation is performed with a lower concentration acid with fewer drops added at a time and for more times to avoid sample loss from the silver boat by
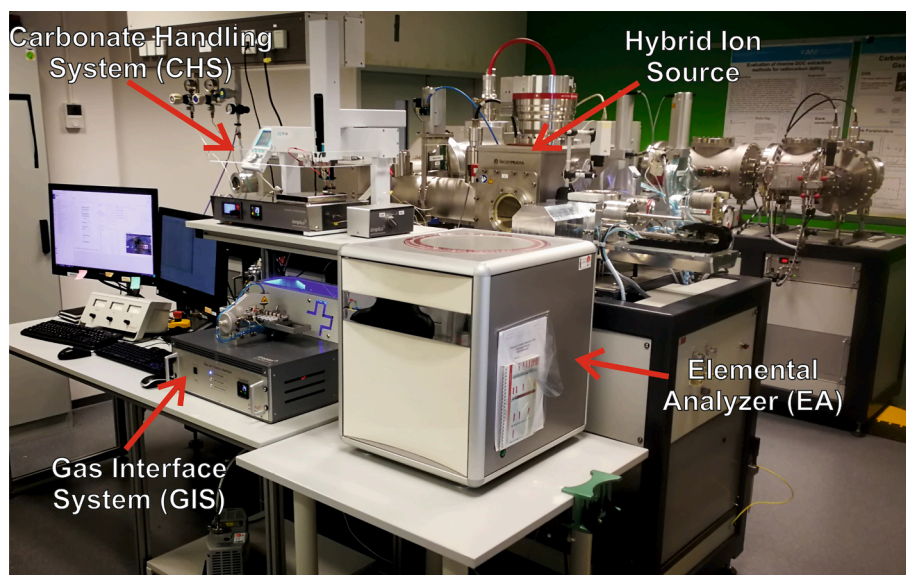

Fig. 1. Photograph of the AWI MICADAS setup, highlighting the major peripheral systems (Carbonate Handling System (CHS) and Elemental Analyzer (EA)) attached to the hybrid ion source via the Gas Interface System (GIS) used in routine ^{14}C analysis.

Table 1

EA combustion media used in routine Analysis. All parts are purchased from ELEMENTAR.

Material	Size	Part #
Small tin boat	4x4x11 mm	22 137 218
Large tin boat	6x6x12 mm	22 137 419
Small silver boat	6x6x12 mm	22 133 212
Large silver boat	8x8x12 mm	22 133 213
Small tin liquid capsule	0.025 mL	03 951 620
Large tin liquid capsule	0.05 mL	S03 951 619

vigorous bubbling. The silver boat becomes brittle in the decarbonation process and is prone to breaking while folding, therefore, after decarbonation the sample in the sliver boat is folded into a tin boat. The tin additionally serves as a catalyst for the combustion process at 950 °C in the EA, which may be connected to the AGE and turned into graphite or directly connected to the GIS. The radiocarbon data are normalized and blank corrected against size matched OxAII and PhA packed in the same silver and tin boats. Secondary, laboratory internal, standards of modern (Kuhgraben) and fossil (Messel Shale) sediments are processed alongside the samples to confirm data reliability and monitor the sample processing contamination.

3.1.2. Wood and plant fragments

Organic material such as wood, plant, charcoal and peat samples are prepared through the standard chemical pretreatment of acid-base-acid (also known as acid-alkali-acid) treatment [17]. Samples are put in glass vials, immersed in 1 M distilled HCl, and covered for 30 min in a 60 °C oven. Samples are then centrifuged; the acid is removed and the samples are rinsed with deionized and decarbonated water. Subsequently, 1 M sodium hydroxide (NaOH) is added to each sample and they are left to sit at 60 °C for 30 min. The samples are then centrifuged, the base is removed and the procedure is repeated up to 20 times or until the base remains colorless after 30 min reaction time. The samples are then rinsed with deionized and decarbonated water and undergo one final acid treatment. After 30 min the samples are rinsed to neutral and dried overnight in a 40 °C oven. Dry samples are weighed and packed into tin boats (Table 1) to be combusted in the EA at 950 °C. The resulting gas may be directed to the AGE for graphitization or to the GIS for direct measurement in the MICADAS. The radiocarbon data are normalized and blank corrected against size matched OxAII and PhA packed in the same tin boats. A secondary wood standard (IAEA-C5) is processed alongside the samples to confirm data reliability and monitor the sample processing contamination.

3.1.3. Particulate organic carbon (POC) on glass-fiber filters

Glass-fiber filters are placed into individual petri dishes and acidified with drops of 10% distilled HCl (just enough to wet the entire filter). The petri dish lids are left slightly ajar and the filters are placed in a 40 °C oven to dry completely. Once dry, the filters are sometimes cut, depending on the amount of carbon on the filter, or used as a whole and folded/rolled into large tin boats (Table 1). These tiny cigar shaped packages are then pressed into a small package using a manual press and die. Non-saline samples (e.g., from lakes or rivers) are burned in the EA equipped with a conventional CuO-reactor set-up at 950 °C, whereas

marine samples are processed using a modified tungsten oxide (WO_3) reactor at 850 °C and Inconel liner to protect the quartz tube from breaking. The produced CO_2 is directly injected to the MICADAS via the GIS. Due to the lack of appropriate standard and blank material, the radiocarbon data are normalized and blank corrected against analyses of standard gases. Processing blank correction is performed afterwards. The processing blank is determined by combusting blank filters treated alongside the samples.

3.1.4. Purified organic compounds

Compound-specific analyses of lipid biomarkers like long-chain *n*-alkanoic acids, or *n*-alkanes are routinely performed. Purified compounds isolated using previously described methods (e.g., [10]) are quantified and checked for purity, with samples containing ideally 50–100 μgC and <1% impurities. These compounds are dissolved in dichloromethane (DCM) at a concentration of approximately 2 μgC/μL and transferred in solution to small tin liquid capsules (25 μL volume, Table 1) kept in a custom-made aluminum tray. The aluminum tray is placed on a hot plate at 40 °C until samples are dried. The process is repeated 3 times to ensure quantitative sample transfer. Subsequently, tin capsules are manually folded using cleaned forceps and combusted at 950 °C in the EA directly connected to the GIS. Due to the lack of appropriate standard and blank material, the radiocarbon data are normalized and blank corrected against standard (OxAII) and blank (PhA) CO_2 gas. Processing blank determination and correction is performed afterwards following a previously described protocol [18].

3.1.5. Freshwater dissolved organic carbon (DOC)

Freshwater DOC samples are obtained by filtration through pre-combusted glass-fiber filters (0.45 or 0.75 μm nominal pore size) and acidified (pH ~ 1, with HCl). For ^{14}C analysis, freshwater volumes containing approximately 100 μgC are dried using a rotary-evaporator. Isolated DOC is re-dissolved in MilliQ at a concentration of ~ 1 μgC/μL, transferred in solution to large tin liquid capsules (50 μL volume, Table 1) and kept in a custom-made Teflon tray. The samples are kept until complete dryness in a desiccator under a mild vacuum at 60 °C. The process is repeated 3 times to ensure quantitative sample transfer. Subsequently, tin capsules are manually folded and combusted at 950 °C in the EA directly connected to the GIS. Due to the lack of appropriate standard and blank material, the radiocarbon data are normalized and blank corrected against standard (OxAII) and blank (PhA) CO_2 gas. Processing blank correction is performed afterwards following a previously described protocol [18].

3.2. Carbonate hydrolyzation using the carbonate handling system (CHS)

Carbonate samples, most commonly foraminifera, are weighed into septum sealed vials to contain 20–100 μgC (for gas) or 0.4-1 mgC (for graphite). The samples are processed using the carbonate handling system (CHS, Ionplus). The sample vials are flushed for 5 min with 70 mL/min ultra-pure Helium to remove any traces of atmospheric CO_2 by a two-way needle. Afterwards 200 μL (for gas) or 1 mL (for graphite) of phosphoric acid (≥85%, Fluka 30417) are added and the hydrolyzation reaction of carbonates to CO_2 takes place over ~ 30 min at 70 °C. Following complete hydrolyzation sample CO_2 is flushed from sample

Table 2

Summary of blank values obtained for routine analysis of graphite samples (400 – 1000 μgC and gas samples (~100 μgC) since 2018.

Blank Material Medium	Measured as graphite $F^{14}C \pm$ stdev	Conv. ^{14}C age [a]	(n)	Measured as gas $F^{14}C \pm$ stdev	Conv. ^{14}C age [a]	(n)
PhA blank gas	n.a.			0.0036 ± 0.0017	45,954	(421)
PhA small tin	0.0019 ± 0.0011	50,511	(127)	0.0075 ± 0.0015	39,453	(58)
PhA silver + tin	0.0046 ± 0.0041	43,337	(280)	0.0259 ± 0.0176	31,598	(38)
IAEA-C1	0.0018 ± 0.0008	51,417	(29)	0.0028 ± 0.0012	47,665	(29)
Pre-Eemian Foraminifera	0.0034 ± 0.0011	45,638	(22)	0.0052 ± 0.0016	42,476	(315)

vials for 1 min at 70 mL/min He flow. The sample gas stream passes over a phosphorus pentoxide trap to remove water vapor and CO_2 is concentrated on the zeolite trap of the GIS for direct injection into the MICADAS or on the zeolite trap of the AGE for graphitization.

Mollusc shells receive the same treatment as foraminifera except that they first undergo a surface etching before they are weighed. Possible surface contamination by debris (common with gastropods) is removed with deionized water in an ultrasonic bath. All shells are then etched in 1% HCl for 30 to 60 s, depending on shell thickness, rinsed to neutral with deionized and decarbonated water and dried overnight in a 60 °C drying oven.

The radiocarbon data are normalized against standard gas (for gas) or OxAII (EA processed graphite targets). Blank correction of foraminifera samples is performed against sample size-matched blank foraminifera (pre-Eemian age carbonate fraction from GeoB3316-1, 521–541 cm > 150 μm; see below). For mollusc shells, size matched preparations of IAEA-C1 are used for blank corrections.

4. Results and performance

4.1. Blanks

4.1.1. Graphite

Machine and sample processing blanks for graphite targets are continuously monitored by preparing blank samples using synthetic PhA packed and combusted identically to the unknown samples. For graphitization, the semi-automated AGE system interfaced with the EA is used.

Systematic differences are observed between blank samples combusted in small tin boats (Table 1), which yield the lowest blank (Table 2), and larger tin boats or combinations of silver and tin boats used for samples that are decarbonated by addition of HCl. Average blank values are reported in Table 2 and translate to blank ages for combusted and graphitized samples of close to 50 ^{14}C ka for samples processed in small tin boats, and to approximately 43 ^{14}C ka for samples combusted in a combination of a silver boat in a larger tin boat. These values are similar to previously reported values of other MICADAS facilities [14,19]. Under ideal conditions, i.e., right after ion source maintenance and using a new batch of PhA values as low as 55 ^{14}C ka can be obtained. Carbonate certified reference material IAEA-C1 yielded a blank of $F^{14}C = 0.0018$ translating to a detection limit for carbonate graphite targets of around 51 ^{14}C ka.

4.1.2. Gas

The machine and sample processing background for gas samples is continuously assessed and corrected. The blanks determined since the start of routine operations in 2018 are strongly method dependent and are summarized in Table 2. Blanks determined directly from the blank gas bottle average $F^{14}C = 0.0036$ (~46 ^{14}C ka). Routinely, blank material is sized-matched to the samples where appropriate blank material is available. For samples of sediment or plant remains, size-matched aliquots of PhA are prepared, packed and combusted identically to samples. Mean values in small tin boats amount to radiocarbon values equivalent to approximately 39.5 ^{14}C ka. For carbonate samples, sized-matched preparations of reference materials IAEA-C1 are processed as blank without chemical pre-treatment using the CHS method described above, yielding a blank age of close to 47.7 ^{14}C ka. This blank value is similar to those reported for other MICADAS systems using the CHS-GIS setup [3,14,20,21].

4.2. Processing blank corrections

Foraminifera are the most commonly analyzed carbonate samples at AWI MICADAS. Processing blanks for foraminifera samples may derive from acid hydrolysis of the carbonates in the semi-automated CHS, reflected also in the values obtained for IAEA-C1. Additionally, it has been shown that contamination of the carbonate fossils, mainly from atmospheric CO_2 adsorbed on the porous surfaces of foraminifera, is the largest source of blank found in foraminifera samples [20,22]. We estimate this blank using the laboratory standard obtained from the > 150 μm size fraction of sediment from a tropical marine sediment core (GeoB3316-1, 521–541 cm), which is of pre-Eemian age and consists almost exclusively of foraminifera tests (Table 2). Different from some other laboratories, we do not perform chemical pre-treatment or leaching steps on foraminifera samples or standards. The pre-Eemian foraminifera measurements are processed as blanks without chemical pre-treatment and are not blank corrected against IAEA-C1, PhA or blank gas. We find that graphite and gas targets contain a combined blank including machine background, sample processing and contamination on the surface of the shells of $F^{14}C = 0.0034$ and 0.0052, respectively, translating into maximum conventional ^{14}C ages of foraminiferal samples of better than 45 and 42 ka for graphite and gas (Table 2), comparable to values reported from other MICADAS facilities [4,20,21].

Routinely, we use size-matched foraminifera blanks to correct $F^{14}C$ values obtained from unknown foraminifera samples, assuming that surface contamination by adsorbed CO_2 should be equivalent between the standard and the unknown samples. Alternative approaches suggest that a leaching step performed using the CHS system might help to remove surface contamination. According to Bard et al. (2015) [14], leaching of several carbonate samples (corals and foraminifera) ranging in $F^{14}C$ between 0.008 and 0.443 for the untreated samples did not result in significantly different $F^{14}C$ results of the leached residue relative to the untreated sample. By contrast, Ausín et al. [23] suggest that a leaching step is needed to remove surface contamination particularly for older samples, and Fagault et al. [21] reported consistently better blanks for leached foraminifera and carbonate blanks. A systematic comparison between the two approaches to account for surface contamination is pending.

For additional applications (e.g., POC on glass-fiber filters, freshwater DOC or purified compounds) no blank material is available and a secondary blank correction via directly (POC) or indirectly (freshwater DOC, purified compounds) determined background contaminations is performed [18,24]. Where a secondary blank correction is necessary, PhA blank gas is used to determine the instrument blank.

The background for purified organic compound samples is determined routinely using the approach described by Sun et al. [18]. Under the assumption of constant background mainly derived from the combustion process, samples of *n*-alkanoic acids extracted from a modern (apple peel collected in 2013) and fossil (Messel shale) are processed as methyl esters (fatty acid methyl esters, FAMEs). Several subsamples with C contents ranging typically between 10 and 70 μgC are processed, and the mass and $F^{14}C$ of the blank is determined using a Bayesian linear regression model [18]. Through this method, $F^{14}C$ and mass of the background C can be estimated and associated with an uncertainty estimate. Typical background estimates are $F^{14}C = 0.5480 \pm 0.0351$ and 1.9 ± 0.1 μgC.

The background for freshwater DOC analysis follows the same principle. Sub-samples of OxAII and PhA were dissolved in MilliQ to contain 10 – 100 μgC and processed as described above (Roto-evaporation, transfer to large tin liquid capsules, and combustion in the EA). The $F^{14}C$ and mass of the blank for freshwater DOC processing is calculated according to Sun et al. [18] and is typically $F^{14}C = 0.7908 \pm 0.0373$ and 2.3 ± 0.1 μgC.

4.3. Reference standards

International reference standard materials as well as three laboratory internal standard materials are routinely analyzed as graphite and gas targets along with unknown samples and processed according to the methodology described above. Results obtained for these materials are summarized in Table 3 and illustrated in Fig. 2. Note that for NIST OxAII, which is routinely used for normalization of the ^{14}C values

Table 3

Summary of $F^{14}C$ values obtained for international certified and laboratory internal standard materials processed as graphite (400 – 1000 µgC) and gas (~100 µgC) samples following material specific blank correction. Note that for NIST OxAII, only values for aliquots of this material processed and treated as unknown sample are reported.

Reference Material Certified Standards	Reference $F^{14}C$	Measured $F^{14}C$ ± stdev (n)			
		graphite		gas	
NIST OxAII	1.3407 ± 0.0005	1.3384 ± 0.0027	(10)	1.3454 ± 0.0063	(10)
NIST OxAI	1.04	1.0398 ± 0.0016	(5)	1.0427 ± 0.0051	(5)
IAEA-C2	0.4114 ± 0.0003	0.4111 ± 0.0027	(23)	0.4103 ± 0.0039	(12)
IAEA-C4	0.0020–0.0044	0.0020 ± 0.0014	(7)	n.a.	
IAEA-C5	0.2305 ± 0.0002	0.2300 ± 0.0015	(60)	0.2287 ± 0.0044	(36)
IAEA-C7	0.4935 ± 0.0012	0.4960 ± 0.0021	(17)	0.4939 ± 0.0038	(10)
Laboratory Standards					
Messel Shale		0.0009 ± 0.0021	(92)	<0.0036	(16)
Kuhgraben sediment		0.8483 ± 0.0057	(98)	0.8426 ± 0.0150	(20)
CAHII Coral[#]	*0.9444 ± 0.0019*[#]	0.9436 ± 0.0019	(10)	0.9394 ± 0.0061	(47)

[#] CAHI Coral Standard provided by Ellen Druffel; the reference value cited here is the average of $n = 294$ analyses of this material performed at Keck Carbon Cycle Radiocarbon Laboratory, UC Irvine.

obtained by AMS, we only report results for analytical runs during which aliquots of the material were treated as unknown samples and results were processed accordingly. The carbonate standard- (IAEA-C2) was subjected to acid hydrolysis using the CHS interfaced with the AGE graphitization unit or the GIS.

Wood and oxalic acid standards (NIST OxAI and OxAII, IAEA-C4, C5, and C7) were packed in tin boats and processed using the EA-AGE or EA-GIS setup. Prior to packing and combustion, IAEA-C5 samples were subjected to acid-base-acid pre-treatment (see above method details). Overall, the values we obtained are in excellent agreement with the reference values for NIST OxAI and OxAII and IAEA-C2 and C5, and within the interval of reported values for IAEA-C4. The value for IAEA-C7 analyzed as graphite deviates more strongly from the consensus value. This might be due to the fact that all values reported here stem from the initial phase of operation in early 2017.

Processing blanks for samples of total organic matter in sediments are further assessed using two laboratory standard materials that are processed along with each sample batch (Table 3, Fig. 3). One of these standard materials is organic-rich Eocene age oil shale from Messel (kindly provided by Dr. Sonja Wedmann, Senckenberg – Leibnitz Institution for Biodiversity and Earth System Research), which was ground and homogenized. After correction for machine (and graphitization) blank using PhA, the mean $F^{14}C$ value for graphite and gas targets from Messel Shale is 0.0009, equivalent to a blank age beyond 56 ^{14}C ka, and below detection limit (older than 45.9 ka), respectively. If only graphite targets containing 1 ± 0.02 mgC are considered, the Messel shale blank is as low as $F^{14}C = 0.0005$, pushing the blank age back to beyond 60 ^{14}C ka.

The true age of the second laboratory standard obtained from sampling the surface sediment of a local creek in Bremen named
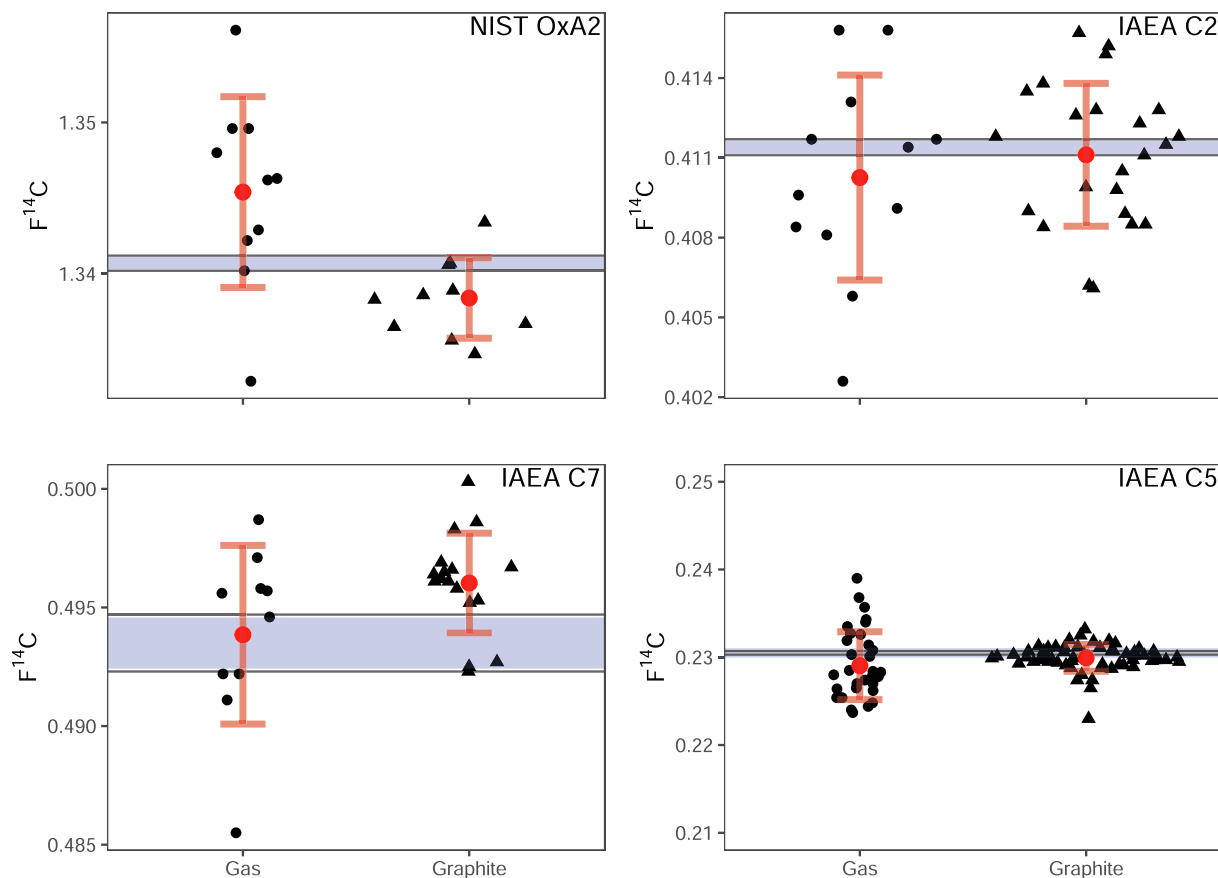

Fig. 2. Sina plot [25] illustrating the jitter of measured $F^{14}C$ values for international reference standards analyzed as gas (black circles) and graphite (black triangles). Material and method specific $F^{14}C$ averages (red circles) and standard deviations (red bars) are shown together with the range of consensus values (blue bars) on $F^{14}C$ axes scaled to fit the scatter of the results.
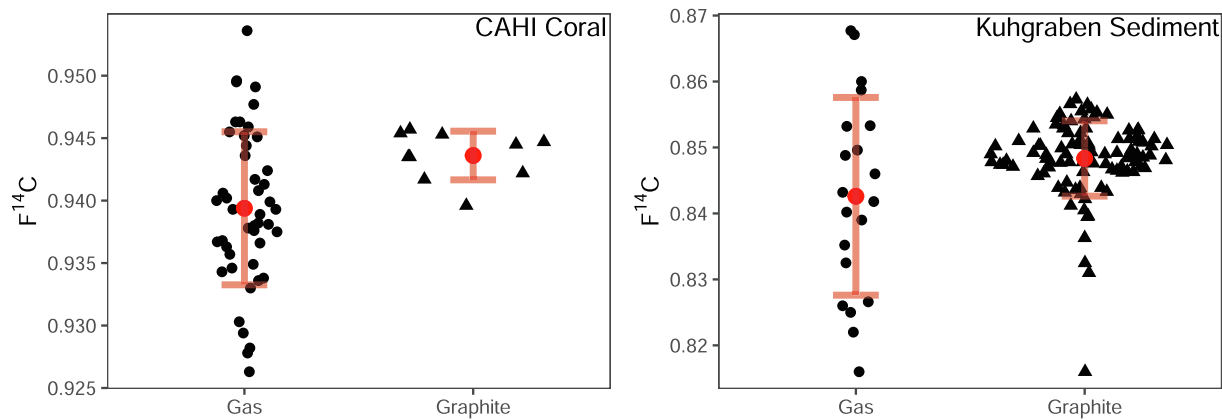
Fig. 3. Sina plot [25] illustrating the jitter of measured $F^{14}C$ values for laboratory internal standards analyzed as gas (black circles) and graphite (black triangles). Material and method specific $F^{14}C$ averages (red circles) and standard deviations (red bars) are shown on independent $F^{14}C$ axes scaled to fit the scatter of the results.

"Kuhgraben", which was dried, milled, and homogenized is unknown. The standard deviation of 98 graphite targets obtained from this submodern standard is 0.0057, which can serve as an estimate of the precision of $F^{14}C$ values obtained from samples within this age range. The precision of 20 measurements as gas is significantly lower (±0.0150) highlighting the larger uncertainty of gas measurements compared to graphite analysis as a result from counting statistics.

The quality of measurements on carbonates is controlled by frequent analysis of a carbonate laboratory standard (Table 3, Fig. 3). The true $F^{14}C$ of the ground and homogenized CAHII Coral standard (kindly provided by Prof. Ellen Druffel, University of California Irvine) is constrained by 294 analyses of this material performed at Keck Carbon Cycle Radiocarbon Laboratory which resulted in an average $F^{14}C$ of 0.9444 (E. Druffel, UC Irvine, personal communication, Table 3). Our repeat analyses thus help to monitor the instrument performance, as well as the reliability and precision of the CHS-GIS methodology. On average the measured $F^{14}C$ of the CAHII Coral standard measured as graphite and gas are comparable and agree with the average from the Keck facility ($F^{14}C_{graphite} = 0.9436$ compared to $F^{14}C_{gas} = 0.9394$). In general, the precision of measurements on young carbonates is better compared to bulk OM (Kuhgraben sediment), but again the precision is lower for small gas samples compared to graphite targets (±0.0061 for gas compared to ± 0.0019 for graphite).

As isotopic fractionation can occur during sample processing, in the sputter ion source or any part of the AMS instrument, $\delta^{13}C$ values are obtained for every measurement and are used for the automatic isotopic fractionation correction routine of the BATS processing software. Table 4 summarizes the mean $\delta^{13}C$ and standard deviations for a suite of international reference materials. In spite of the potential fractionation

effects, the mean of $\delta^{13}C$ values measured as graphite or gas are, in general, accurate and within $\sim$ 1‰ range of the certified reference values (comparable to findings of Szidat et al. (2014) [19] and Bard et al. (2015) [14]), except for IAEA-C2 measured as gas, for which the mean differs significantly (by > 5‰) from the reference value. The reason remains unknown but could be related to the carbonate specific CHS-GIS method employed and will be further investigated. The precision of $\delta^{13}C$ MICADAS measurements, however, is poor. The standard deviation is mostly >1‰ (worst for IAEA-C2 measured as graphite with 3.5‰), previously shown to be achievable by other MICADAS laboratories for standard samples processed as graphite [14,19]. Since we considered samples whithin a relatively large size range of 400–1000 µgC, we speculate that part of the observed larger standard deviation might stem from isotopic fractionation during (incomplete) graphitization [26]. Likewise, small differences in the length of gas sample measurements might account for additional isotopic fractionation. Therefore, the MICADAS derived stable carbon isotope data are not as precise and accurate as values obtained by conventional isotope ratio mass spectrometry (IRMS) and should not be used for scientific interpretation. Nevertheless, we are investigating the reasons for the poor $\delta^{13}C$ precision of our MICADAS and aim to improve the data quality in the near future.

5. Conclusion and outlook

The radiocarbon laboratory at AWI Bremerhaven is equipped with a MICADAS with a hybrid ion source allowing reliable and precise ^{14}C analyses on CO_2 gas and graphite samples. Accuracy and precision were assessed using certified reference standard materials and laboratory internal processing standards. Good agreement was obtained with published consensus values, similar to reports from other MICADAS systems. Detection limits vary between sample materials and gas or graphite targets as well as with sample size. For graphite (gas) targets of carbonates and bulk sedimentary organic matter, detection limits were > 51 (47) and > 50 (39) ^{14}C ka BP. Small foraminifera samples processed as gas are the most frequently analyzed sample type with a detection limit of around 42 ^{14}C ka BP. The poorer precision of small samples measured as gas compared to conventional graphite led to the decision that, whenever possible, organic matter samples are to be processed as graphite targets. Especially for bulk organic matter this is feasible, and advisable, as sample material is rarely restricted. For carbonates the precision of gas analysis is better and allows to report reliable datasets (for instance for sediment stratigraphy) even if carbonate micro-fossils are scarce.

Table 4
Summary of $\delta^{13}C$ values obtained for international certified standard materials processed as graphite (400 – 1000 µgC) and gas (~100 µgC) samples following material specific blank correction.

Reference Material Certified Standards	Reference $\delta^{13}C$ [‰ PDB]	Measured $\delta^{13}C \pm$ stdev [‰ PDB] (n)			
		graphite		gas	
NIST OxAII	−17.8 ± 0.1	−16.8 ± 1.2	(10)	−17.9 ± 1.7	(10)
NIST OxAI	−19.3	−19.0 ± 0.4	(5)	−20.5 ± 1.3	(5)
IAEA-C2	−8.3 ± 0.3	−8.1 ± 3.5	(23)	−13.5 ± 2.8	(12)
IAEA-C5	−25.5 ± 0.7	−24.6 ± 2.8	(60)	−26.1 ± 1.8	(36)
IAEA-C7	−14.5 ± 0.2	−14.1 ± 1.8	(17)	−15.9 ± 1.7	(10)

CRediT authorship contribution statement

Gesine Mollenhauer: Conceptualization, Formal analysis, Supervision, Project administration, Funding acquisition, Writing - original draft. **Hendrik Grotheer:** Formal analysis, Data curation, Validation, Visualization, Writing - review & editing. **Torben Gentz:** Methodology, Formal analysis, Data curation, Validation, Writing - review & editing. **Elizabeth Bonk:** Methodology, Writing - review & editing. **Jens Hefter:** Methodology, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] H.-A. Synal, M. Stocker, M. Suter, MICADAS: A new compact radiocarbon AMS system, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 259 (2007) 7–13. 10.1016/j.nimb.2007.01.138.

[2] S.M. Fahrni, L. Wacker, H.A. Synal, S. Szidat, Improving a gas ion source for 14C AMS, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 294 (2013) 320–327. 10.1016/j.nimb.2012.03.037.

[3] L. Wacker, S.M. Fahrni, I. Hajdas, M. Molnar, H.-A. Synal, S. Szidat, Y.L. Zhang, A versatile gas interface for routine radiocarbon analysis with a gas ion source, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 294 (2013) 315–319, https://doi.org/10.1016/J.NIMB.2012.02.009.

[4] L. Wacker, R.H. Fülöp, I. Hajdas, M. Molnár, J. Rethemeyer, A novel approach to process carbonate samples for radiocarbon measurements with helium carrier gas, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 294 (2013) 214–217, https://doi.org/10.1016/j.nimb.2012.08.030.

[5] H. Grotheer, V. Meyer, T. Riedel, G. Pfalz, L. Mathieu, J. Hefter, T. Gentz, G. Mollenhauer, M. Fritz, Burial and origin of permafrost derived carbon in the nearshore zone of the southern Canadian Beaufort Sea, Geophys. Res. Lett. (2020), https://doi.org/10.1029/2019GL085897.

[6] B. Wei, G. Mollenhauer, J. Hefter, H. Grotheer, G. Jia, Dispersal and aging of terrigenous organic matter in the Pearl River Estuary and the northern South China Sea Shelf, Geochim. Cosmochim. Acta. 282 (2020) 324–339, https://doi.org/10.1016/j.gca.2020.04.032.

[7] S.A. Vyse, U. Herzschuh, A.A. Andreev, L.A. Pestryakova, B. Diekmann, S. J. Armitage, B.K. Biskaborn, Geochemical and sedimentological responses of arctic glacial Lake Ilirney, chukotka (far east Russia) to palaeoenvironmental change since ~51.8 ka BP, Quat. Sci. Rev. 247 (2020), https://doi.org/10.1016/j.quascirev.2020.106607.

[8] T. Opel, J.B. Murton, S. Wetterich, H. Meyer, K. Ashastina, F. Günther, H. Grotheer, G. Mollenhauer, P.P. Danilov, V. Boeskorov, G.N. Savvinov, L. Schirrmeister, Past climate and continentality inferred from ice wedges at Batagay megaslump in the Northern Hemisphere's most continental region, Yana Highlands, interior Yakutia, Clim. Past. 15 (2019) 1443–1461. 10.5194/cp-15-1443-2019.

[9] [9] L. Sander, R. Michaelis, S. Papenmeier, S. Pravkin, G. Mollenhauer, H. Grotheer, T. Gentz, K.H. Wiltshire, Indication of Holocene sea-level stability in the southern Laptev Sea recorded by beach ridges in north-east Siberia, Russia, Polar Res. 38 (2019) 1–13. 10.33265/polar.v38.3379.

[10] V.D. Meyer, J. Hefter, P. Köhler, R. Tiedemann, R. Gersonde, L. Wacker, G. Mollenhauer, Permafrost-carbon mobilization in Beringia caused by deglacial meltwater runoff, sea-level rise and warming, Environ. Res. Lett. 14 (2019), https://doi.org/10.1088/1748-9326/ab2653.

[11] K. Küssner, M. Sarnthein, F. Lamy, R. Tiedemann, High-resolution radiocarbon records trace episodes of Zoophycos burrowing, Mar. Geol. 403 (2018) 48–56, https://doi.org/10.1016/j.margeo.2018.04.013.

[12] T.A. Ronge, M. Prange, G. Mollenhauer, M. Ellinghausen, G. Kuhn, R. Tiedemann, Radiocarbon Evidence for the Contribution of the Southern Indian Ocean to the Evolution of Atmospheric CO2 Over the Last 32,000 Years, Paleoceanogr. Paleoclimatology. 35 (2020), https://doi.org/10.1029/2019PA003733.

[13] J. Wu, R. Stein, K. Fahl, G. Mollenhauer, W. Geibert, N. Syring, S.-I. Nam, Deglacial to Holocene variability in surface water characteristics and major floods in the Beaufort Sea, Commun. Earth Environ. (2020), https://doi.org/10.1038/s43247-020-00028-z.

[14] E. Bard, T. Tuna, Y. Fagault, L. Bonvalot, L. Wacker, S. Fahrni, H.A. Synal, AixMICADAS, the accelerator mass spectrometer dedicated to14C recently installed in Aix-en-Provence, France, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 361 (2015) 80–86, https://doi.org/10.1016/j.nimb.2015.01.075.

[15] L. Wacker, M. Christl, H.A. Synal, Bats: A new tool for AMS data reduction, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 268 (2010) 976–979. 10.1016/j.nimb.2009.10.078.

[16] L. Wacker, M. Němec, J. Bourquin, A revolutionary graphitisation system: Fully automated, compact and simple, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 268 (2010) 931–934. 10.1016/j.nimb.2009.10.067.

[17] H. De Vries, G.W. Barendsen, Measurements of age by the carbon-14 technique, Nature. 174 (1954) 1138–1141, https://doi.org/10.1038/1741138a0.

[18] S. Sun, V.D. Meyer, A.M. Dolman, M. Winterfeld, J. Hefter, W. Dummann, C. McIntyre, D.B. Montluçon, N. Haghipour, L. Wacker, T. Gentz, T.S. Van Der Voort, T.I. Eglinton, G. Mollenhauer, 14C Blank Assessment in Small-Scale Compound-Specific Radiocarbon Analysis of Lipid Biomarkers and Lignin Phenols, Radiocarbon. 62 (2020) 207–218. 10.1017/RDC.2019.108.

[19] S. Szidat, G.A. Salazar, E. Vogel, M. Battaglia, L. Wacker, H.-A. Synal, A. Türler, 14C Analysis and Sample Preparation at the New Bern Laboratory for the Analysis of Radiocarbon with AMS (LARA), Radiocarbon. 56 (2014) 561–566, https://doi.org/10.2458/56.17457.

[20] [20] J. Gottschalk, S. Szidat, E. Michel, A. Mazaud, G. Salazar, M. Battaglia, J. Lippold, S.L. Jaccard, Radiocarbon measurements of small-size foraminifer samples with the MIni CArbon DAting System (MICADAS) at the University of Bern: implications for paleoclimate reconstructions, Radiocarbon. (2018) in press. 10.1017/RDC.2018.3.

[21] Y. Fagault, T. Tuna, F. Rostek, E. Bard, Radiocarbon dating small carbonate samples with the gas ion source of AixMICADAS, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 455 (2019) 276–283, https://doi.org/10.1016/j.nimb.2018.11.018.

[22] M. Schleicher, P.M. Grootes, M.J. Nadeau, A. Schoon, The carbonate 14C background and its components at the Leibniz AMS facility, Radiocarbon. 40 (1998) 85–93, https://doi.org/10.1017/s0033822200017926.

[23] B. Ausín, N. Haghipour, L. Wacker, A.H.L. Voelker, D. Hodell, C. Magill, N. Looser, S.M. Bernasconi, T.I. Eglinton, Radiocarbon Age Offsets Between Two Surface Dwelling Planktonic Foraminifera Species During Abrupt Climate Events in the SW Iberian Margin, Paleoceanogr. Paleoclimatology. 34 (2019) 63–78, https://doi.org/10.1029/2018PA003490.

[24] J. Hwang, E.R.M. Druffel, Blank correction for d14C measurements in organic compound classes of oceanic particulate matter, Radiocarbon. 47 (2005) 75–87.

[25] N. Sidiropoulos, S.H. Sohi, T.L. Pedersen, B.T. Porse, O. Winther, N. Rapin, F. O. Bagger, SinaPlot: An Enhanced Chart for Simple and Truthful Representation of Single Observations Over Multiple Classes, J. Comput. Graph. Stat. 27 (2018) 673–676, https://doi.org/10.1080/10618600.2017.1366914.

[26] S.M. Fahrni, J.R. Southon, G.M. Santos, S.W.L. Palstra, H.A.J. Meijer, X. Xu, Reassessment of the 13C/12C and 14C/12C isotopic fractionation ratio and its impact on high-precision radiocarbon dating, Geochim. Cosmochi. Acta 213 (2017) 330–345, https://doi.org/10.1016/j.gca.2017.05.038.