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## THE RADIOCARBON SAMPLE ARCHIVE OF TRONDHEIM

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**ABSTRACT.** Atmospheric CO<sub>2</sub> samples have been collected by the Trondheim Radiocarbon Laboratory since the 1960s. The remaining material from the measurements has been precipitated as CaCO<sub>3</sub> and stored in glass containers. We investigated some of the stored samples to assess whether the material could still be used for remeasurements of atmospheric radiocarbon (<sup>14</sup>C) content, or if it has been contaminated during the years of storage. We attempted different methods to clean the carbonate and release the CO<sub>2</sub> for new measurements. The results indicate that the older samples before 1970 show a significant change in <sup>14</sup>C content compared to the original measurements, and that our cleaning methods have only little effect. Later samples from the 1970s, which were archived in glass containers with a different lid, show a lower contamination that, however, still leads to an added uncertainty of several pMC and makes these samples unreliable.

**KEYWORDS:** AMS, radiocarbon, radiocarbon AMS dating.

## INTRODUCTION

Reidar Nydal, from the Trondheim Radiocarbon Laboratory, became interested in tracing bomb radiocarbon (<sup>14</sup>C) in the atmosphere (Nydal and Lövseth 1983):

in 1961 when great atmospheric test series were performed at higher northern latitudes, mainly at Novaya Zemlya (. . .). The very high concentration of <sup>14</sup>C in a relatively limited area of the globe at higher northern latitudes gave a better opportunity than earlier to study the exchange of <sup>14</sup>C between various parts of the atmosphere and between the atmosphere and other reservoirs in nature. A number of ground stations were established for the purpose between Spitsbergen and Madagascar (. . .). In most cases more samples were collected at each station than were immediately necessary for measurement, especially during the 1960's. It has been regarded as very important to conserve some extra samples in case there should be need for them. It could also be possible that one would wish to repeat some measurements with higher accuracy in the future.

This resulted in a carbonate archive of atmospheric <sup>14</sup>C samples. The different stations, their sampling periods, and measurements are summarized in Figure 1. Out of a total of approximately 2700 samples, about 1600 have been measured and used in a series of publications (Nydal 1963, 1966, 1968; Nydal and Lövseth 1965). The sampling program and data sets were published by (Nydal and Lövseth 1983).

In recent years, the use of <sup>14</sup>C as an atmospheric tracer has gained interest in research, particularly regarding the datasets detailing the global distribution of the <sup>14</sup>C bomb spike over time (Levin and Hesshaimer 2000; Randerson et al. 2002; Hua and Barbetti 2004; Hua et al. 2013, 2021). This prompted us to revisit the Trondheim archive collection. The samples cover a large latitudinal range at a time when the <sup>14</sup>C content of the atmosphere changed very rapidly. In addition, they provide a weekly to monthly resolution throughout the whole year, in contrast

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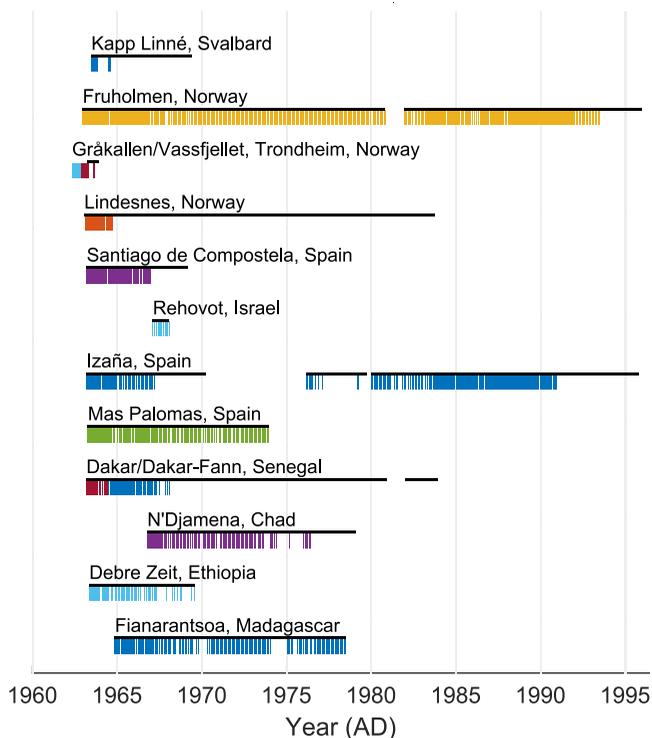


Figure 1 Activity of Nydal's network sorted by latitude of the sampling location. The horizontal bars indicate the sampling periods when samples were registered. The vertical bars indicate the published measurements. The sampling stations are sorted by their geographical latitude (north to south).

to tree rings which record only during the growing season. This makes the collection potentially very valuable to study atmospheric circulation. Not only could the unmeasured samples extend the datasets, remeasurements with modern accelerator mass spectrometry (AMS) would also provide higher precision than the original measurements.

Before measuring a large number of samples, we decided to assess whether the archived samples are still in good condition or whether they have been contaminated over the years of storage by adsorbing atmospheric carbon dioxide ( $\text{CO}_2$ ) or organic compounds. We selected samples from 1963 for maximum  $^{14}\text{C}$  concentrations ( $\approx 180$  pMC) and test sensitivity. We added stored samples from 1980 ( $\approx 130$  pMC) that differed less from ambient atmosphere during a shorter storage period for comparison. Archaeological samples ( $\approx 50$  pMC) were added to repeat the contamination test for samples with a  $^{14}\text{C}$  deficit relative to the ambient atmosphere.

Measurements of most samples were not in statistical agreement with the original measurements, indicating serious contamination. Therefore, we tested whether our standard procedures for cleaning carbonate samples could eliminate the contamination. Here, we report the remeasurements of the archived samples and our efforts to remove the contamination.

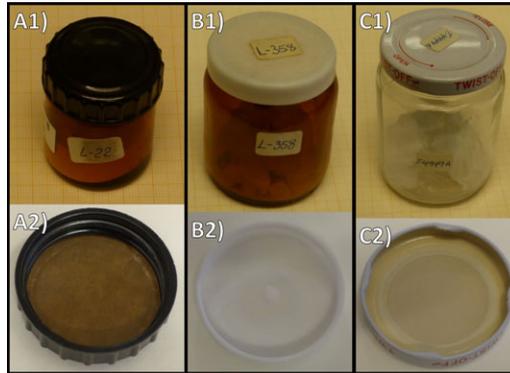


Figure 2 A1) Type 1 container with the inside of the cap (A2). Different sizes were used of this type ranging from the smallest one shown to the same size as the newer models. B1) Type 2 container with its lid (B2). C1) Type 3 container with its metal cap (C2).

## SAMPLES AND METHODS

### Archived Samples

For the Trondheim carbonate archive samples atmospheric  $\text{CO}_2$  was absorbed in a sodium hydroxide ( $\text{NaOH}$ ) solution at the sampling locations, and the final solution was filled into airtight bottles for shipping to the laboratory in Trondheim (Nydal 1963). The samples, then in the form of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ) in aqueous solution, were precipitated as calcium carbonate ( $\text{CaCO}_3$ ) in the laboratory using calcium chloride ( $\text{CaCl}_2$ ) and washed to remove salt. Hydrochloric acid ( $\text{HCl}$ ) was used to release  $\text{CO}_2$  for measurement while the remaining carbonate material was put into storage (Nydal 1966). In addition to the atmospheric samples, some archaeological samples were also archived. Unfortunately, there is only limited information on the samples and their handling. From the sorting of the samples in the archive boxes, it appears that some samples were precipitated shortly after sampling, while others waited several months or even years before being archived, though no precipitation dates have been documented. Some of the samples from the late 1980s and 1990s were not precipitated and were stored in the  $\text{NaOH}$  solution. These samples are not part of the present investigation. However, the ordering could also be due to later tidying up. The sample sizes are not documented, but from our assessment, they vary from about 1 g to over 10 g and some of the samples were stored in up to three containers.

The Trondheim carbonate archive contains samples from the 1960s to the early 1990s. Thus, storage time varies greatly. The samples have been stored in glass jars, but the type of lid has changed over the years. The oldest samples were stored in containers with a hard plastic screw cap with a paper liner, which is mechanically fixed without glue (type 1). Starting around 1970, a type with a flexible squeeze-on plastic lid (type 2) came into use, as well as a version with metal screw cap (type 3) which was used to store archaeological samples (Figure 2). When going through the archive boxes, we noticed that some of the type 1 containers were not, or no longer, tightened properly, so that atmospheric  $\text{CO}_2$  could easily leak into the container. We avoided these when selecting samples for our tests. Some of these samples are stored in multiple containers that we labelled with a suffix letter for later identification. The lids of the type 2

containers are tight on the glass. We did not notice any type 3 containers that were not closed firmly, but there are only few type 3 containers in the archive.

### Sample Selection

We selected 24 atmospheric samples from the period 1963 to 1980 from a site in Lindesnes, a municipality in Southern Norway (58°N) as well as 25 archaeological samples with  $^{14}\text{C}$  concentration from 25 to 94 pMC, prepared between 1963 and 1984, and stored in all three types of containers to check for a potential influence of storage on the samples'  $^{14}\text{C}$  content (Table 1). Three aliquots from sample L-22-B were taken from the top, middle and lowest part of the sample container to investigate whether we can determine a contamination gradient, e.g., penetrating from the lid down.

Some of the samples had been measured by Nydal (Nydal and Lövseth 1983), while the results of the others can be compared to an interpolated value of the two closest Nydal measurements, or to datasets from Vermunt, Austria or Schauinsland in Germany (Levin et al. 1985) (details in Table 1). While the interpolation is not very accurate, this method should work in the period of summer 1963 for which samples it was used, as the Northern Hemisphere zone 1 (NH1) calibration (Hua et al. 2021) curve shows only minor curvature. We think that the Vermunt and Schauinsland datasets (Levin et al. 1985) are best suited for comparison because they are also based on atmospheric sampling, and are the closest of such sites available. As regional differences are occurring, this comparison only gives a general indication whether the results are accurate, but it might be the most comparable in a sense of local influence (Levin et al. 2003).

### Sample Treatment

We used two methods for  $\text{CO}_2$  release. The first one was a thermal “combustion” (950°C) of the carbonate in an elemental analyzer (EA). This will, in addition to the carbonate, also convert organic contaminants into  $\text{CO}_2$ . The  $\text{CO}_2$  gas was reduced to graphite in our automated reduction system using a  $\text{H}_2$ -Fe-reaction (Seiler et al. 2019). In the other method, the samples were prepared in evacuated glass ampoules.  $\text{H}_3\text{PO}_4$  was used to release the  $\text{CO}_2$  from the carbonate only, which was then transferred to our manual Zn-Fe reduction system. Both reduction methods produce equivalent graphite so that the samples can be measured against the same standards and the results can be compared directly (Seiler et al. 2019).

All samples were measured twice at the Trondheim 1 MV AMS system following our standard procedures (Nadeau et al. 2015; Seiler et al. 2019).

As the results of 19 samples prepared both using  $\text{H}_3\text{PO}_4$  and EA were statistically identical, the remaining samples were prepared twice with the EA, which is less labor intensive. Early results indicated that some archived bomb spike samples now show a much lower  $^{14}\text{C}$  content (5–15 pMC difference). Thus, an important question was whether this contamination could be reliably removed.

We tested two different leaching methods to remove contamination from 12 atmospheric and 7 archaeological samples. Firstly, we subjected the samples to 0.5 mL  $\text{H}_2\text{O}_2$  (30%), which should remove potential organic contaminants and leach the surface of the carbonate, removing potentially adsorbed  $\text{CO}_2$ . The samples were kept in  $\text{H}_2\text{O}_2$  for at least 2 hr before further treatment. The other method was a surface leaching with ca. 0.3 mL diluted HCl (1%) wherein

Table 1  $^{14}\text{C}$  content in pMC of untreated carbonate powder. Reference results: O = original measurement, I = linear interpolation between two neighboring original measurements, S = Schauinsland, V = Vermunt. Symbol † indicates a measurement not used in the calculations.

Sample number	Original laboratory number/container #	Start of the 1 week sampling period	$^{14}\text{C}$ content - EA combustion (pMC)	$^{14}\text{C}$ content - $\text{H}_3\text{PO}_4$ hydrolysis (pMC)	Difference between measurements (pMC)	$^{14}\text{C}$ content - average (pMC)	Reference result (pMC)/Reference source	Difference to reference value (pMC)
<b>Atmospheric samples</b>								
TRa-16393	L-22-B/# 1	1963-06-17	171.25 ± 0.30	156.61 ± 0.19†	14.64 ± 0.36†	171.25 ± 0.30	180.40 ± 1.00/O	-9.20 ± 1.04
TRa-16394	L-23-C/#1	1963-06-24	173.53 ± 0.21	174.00 ± 0.15	-0.47 ± 0.26	173.77 ± 0.13	185.00 ± 0.80/I	-11.30 ± 0.81
TRa-16395	L-24/#1	1963-07-01	183.46 ± 0.18	179.07 ± 0.21†	4.39 ± 0.28†	183.46 ± 0.18	189.60 ± 1.20/O	-6.20 ± 1.21
TRa-16396	L-25-B/#1	1963-07-08	184.92 ± 0.26	184.13 ± 0.19	0.79 ± 0.32	184.53 ± 0.16	191.00 ± 0.80/I	-6.50 ± 0.82
TRa-16397	L-26/#1	1963-07-15	184.65 ± 0.18	184.43 ± 0.23	0.22 ± 0.29	184.54 ± 0.15	192.50 ± 1.20/O	-8.00 ± 1.21
TRa-16398	L-27-B/#1	1963-07-22	188.49 ± 0.20	187.57 ± 0.29	0.92 ± 0.35	188.03 ± 0.18	194.40 ± 0.80/I	-6.40 ± 0.82
TRa-16399	L-28/#1	1963-07-29	185.75 ± 0.29	186.79 ± 0.21	-1.04 ± 0.36	186.27 ± 0.18	196.40 ± 1.20/O	-10.20 ± 1.21
TRa-16400	L-29-B/#1	1963-08-05	181.73 ± 0.18	182.09 ± 0.23	-0.36 ± 0.29	181.91 ± 0.15	198.50 ± 0.80/I	-16.60 ± 0.81
				Average	0.04 ± 0.74			-9.16 ± 3.29
TRa-16401	L-358/#2	1980-08-04	127.83 ± 0.16	128.66 ± 0.17	-0.83 ± 0.23	128.25 ± 0.12	127.10 ± 0.60/S	1.10 ± 0.61
TRa-16402	L-359/#2	1980-09-01	127.73 ± 0.15	128.12 ± 0.17	-0.39 ± 0.23	127.93 ± 0.11	127.20 ± 0.60/S	0.70 ± 0.61
TRa-16403	L-360/#2	1980-10-06	128.37 ± 0.14	128.58 ± 0.14	-0.21 ± 0.20	128.48 ± 0.10	127.40 ± 0.60/S	1.00 ± 0.61
TRa-16404	L-361/#2	1980-11-03	127.33 ± 0.17	128.15 ± 0.13	-0.82 ± 0.21	127.74 ± 0.11	126.20 ± 0.60/S	1.50 ± 0.61
				Average	-0.53 ± 0.32			1.08 ± 0.33
Sample number	Original laboratory number/container #	Start of the 1 week sampling period	$^{14}\text{C}$ content - EA combustion 1 (pMC)	$^{14}\text{C}$ content - EA combustion 2 (pMC)	Difference between measurements (pMC)	$^{14}\text{C}$ content - average (pMC)	Reference result (pMC)/Reference source	Difference to reference value (pMC)
TRa-16656	L-187/#1	1967-08-07	161.87 ± 0.18	161.60 ± 0.17	0.27 ± 0.25	161.74 ± 0.12	164.60 ± 0.60/V	-2.90 ± 0.61
TRa-16657	L-188/#1	1967-08-21	163.30 ± 0.18	163.40 ± 0.16	-0.10 ± 0.24	163.35 ± 0.12	164.60 ± 0.60/V	-1.30 ± 0.61
TRa-16658	L-189/#1	1967-09-04	163.25 ± 0.18	163.27 ± 0.29	-0.02 ± 0.34	163.26 ± 0.17	160.30 ± 0.60/V	2.90 ± 0.62
TRa-16659	L-226/#1	1970-04-20	150.77 ± 0.17	150.94 ± 0.16	-0.17 ± 0.23	150.86 ± 0.12	153.10 ± 0.60/V	-2.30 ± 0.61
TRa-16660	L-236/#1	1971-02-01	144.61 ± 0.19	145.09 ± 0.22	-0.48 ± 0.29	144.85 ± 0.15	149.70 ± 0.70/V	-4.90 ± 0.72
TRa-16661	L-259/#1	1972-11-06	144.39 ± 0.19	144.73 ± 0.16	-0.34 ± 0.25	144.56 ± 0.12	146.50 ± 0.50/V	-2.00 ± 0.51
TRa-16663	L-238/#1	1971-03-29	148.16 ± 0.17	148.63 ± 0.18	-0.47 ± 0.25	148.40 ± 0.12	151.00 ± 0.80/V	-2.60 ± 0.81
				Average	-0.15 ± 0.24			-1.87 ± 2.38
TRa-16662	L-232/#2	1970-10-05	153.07 ± 0.19	152.85 ± 0.17	0.22 ± 0.25	152.96 ± 0.13	153.00 ± 0.60/V	-0.10 ± 0.61
TRa-16664	L-252/#2	1972-04-24	146.77 ± 0.19	146.78 ± 0.16	-0.01 ± 0.25	146.78 ± 0.12	147.50 ± 0.60/V	-0.80 ± 0.61
TRa-16665	L-284/#2	1974-10-14	140.63 ± 0.16	141.33 ± 0.22	-0.70 ± 0.27	140.98 ± 0.14	140.50 ± 0.50/V	0.40 ± 0.52
TRa-16666	L-285/#2	1974-11-11	138.99 ± 0.16	139.00 ± 0.20	-0.01 ± 0.26	139.00 ± 0.13	139.30 ± 0.60/V	-0.30 ± 0.61
TRa-16667	L-286/#2	1974-12-09	139.20 ± 0.17	139.10 ± 0.25	0.10 ± 0.30	139.15 ± 0.15	137.00 ± 0.60/V	2.10 ± 0.62
				Average	-0.08 ± 0.36			0.26 ± 1.11

(Continued)

Table 1 (*Continued*)

Sample number	Original laboratory number/Container #	Processing year	<sup>14</sup> C content - EA combustion (pMC)	<sup>14</sup> C content - H <sub>3</sub> PO <sub>4</sub> hydrolysis (pMC)	Difference between measurements (pMC)	<sup>14</sup> C content - Average (pMC)	Reference result (pMC)/Reference source	Difference to reference value (pMC)
<b>Archaeological samples</b>								
TRa-16405	T-363/#1	1963	67.27 ± 0.11	67.56 ± 0.10	-0.29 ± 0.15	67.42 ± 0.07	66.30 ± 0.60/O	1.11 ± 0.60
TRa-16406	T-597/#1	1966	41.62 ± 0.09	42.31 ± 0.08	-0.69 ± 0.12	41.97 ± 0.06	39.90 ± 0.70/O	2.07 ± 0.70
TRa-16408	T-1031/#1	1971	59.68 ± 0.11	59.86 ± 0.10	-0.18 ± 0.15	59.77 ± 0.07	57.20 ± 0.80/O	2.57 ± 0.80
				Average	-0.30 ± 0.26			1.92 ± 0.74
TRa-16409	T-4949A/#3	1983	64.31 ± 0.12	64.72 ± 0.14	-0.41 ± 0.18	64.52 ± 0.09	65.10 ± 0.60/O	-0.59 ± 0.61
TRa-16410	T-5099A/#3	1983	48.95 ± 0.09	49.44 ± 0.10	-0.49 ± 0.13	49.20 ± 0.07	48.80 ± 0.60/O	0.40 ± 0.60
TRa-16411	T-5100A/#3	1983	33.59 ± 0.08	33.78 ± 0.07	-0.19 ± 0.11	33.69 ± 0.05	34.80 ± 0.50/O	-1.11 ± 0.50
TRa-16412	T-5130/#3	1983	43.91 ± 0.10	43.87 ± 0.13	0.04 ± 0.16	43.89 ± 0.08	43.90 ± 0.50/O	-0.01 ± 0.51
				Average	-0.22 ± 0.22			-0.30 ± 0.65
Sample number	Original laboratory number/Container #	Processing year	<sup>14</sup> C content - EA combustion 1 (pMC)	<sup>14</sup> C content - EA combustion 2 (pMC)	Difference between measurements (pMC)	<sup>14</sup> C content - Average (pMC)	Reference result (pMC)/Reference source	Difference to reference value (pMC)
TRa-16668	T-2547/#2	1978	66.79 ± 0.14	66.74 ± 0.18	0.05 ± 0.23	66.77 ± 0.11	65.10 ± 0.30/O	1.67 ± 0.32
TRa-16669	T-2536/#2	1978	47.30 ± 0.09	47.40 ± 0.11	-0.10 ± 0.14	47.35 ± 0.07	46.90 ± 0.50/O	0.45 ± 0.50
TRa-16670	T-2680/#2	1978	63.21 ± 0.11	63.36 ± 0.12	-0.15 ± 0.16	63.29 ± 0.08	59.80 ± 0.70/O	3.49 ± 0.70
TRa-18334	T-2457/#2	1976	94.07 ± 0.12	94.43 ± 0.14	-0.36 ± 0.18	94.25 ± 0.09	97.40 ± 0.80/O	-3.15 ± 0.81
TRa-18335	T-2461/#2	1976	80.95 ± 0.12	81.07 ± 0.13	-0.12 ± 0.18	81.01 ± 0.09	81.20 ± 0.60/O	-0.19 ± 0.61
TRa-18336	T-2663/#2	1977	83.32 ± 0.12	83.64 ± 0.14	-0.32 ± 0.18	83.48 ± 0.09	81.90 ± 0.80/O	1.58 ± 0.81
TRa-18337	T-4719A/#2	1983	41.88 ± 0.1	41.75 ± 0.08	0.13 ± 0.13	41.82 ± 0.06	42.00 ± 0.50/O	-0.18 ± 0.50
TRa-18338	T-4684/#2	1982	78.64 ± 0.13	77.45 ± 0.13	1.19 ± 0.18	78.05 ± 0.09	79.30 ± 0.70/O	-1.25 ± 0.71
TRa-18339	T-4686/#2	1982	90.59 ± 0.12	91.10 ± 0.14	-0.51 ± 0.18	90.85 ± 0.09	89.30 ± 0.80/O	1.55 ± 0.81
TRa-18340	T-4653/#2	1983	88.24 ± 0.12	88.83 ± 0.14	-0.59 ± 0.18	88.54 ± 0.09	89.20 ± 0.40/O	-0.66 ± 0.41
TRa-18341	T-4621/#2	1982	93.11 ± 0.19	92.99 ± 0.14	0.12 ± 0.24	93.05 ± 0.12	95.30 ± 0.70/O	-2.25 ± 0.71
TRa-18342	T-4642A/#2	1983	59.15 ± 0.1	59.54 ± 0.12	-0.39 ± 0.16	59.35 ± 0.08	59.80 ± 0.40/O	-0.45 ± 0.41
TRa-18343	T-4588/#2	1982	30.85 ± 0.08	30.84 ± 0.09	0.01 ± 0.12	30.85 ± 0.06	29.40 ± 0.30/O	1.45 ± 0.31
TRa-18344	T-4597/#2	1982	26.31 ± 0.07	26.32 ± 0.08	-0.01 ± 0.11	26.32 ± 0.05	25.30 ± 0.30/O	1.02 ± 0.30
TRa-18345	T-4570A/#2	1982	62.96 ± 0.14	62.67 ± 0.11	0.29 ± 0.18	62.82 ± 0.09	61.40 ± 0.60/O	1.42 ± 0.61
TRa-18346	T-4549/#2	1981	97.15 ± 0.14	97.38 ± 0.13	-0.23 ± 0.19	97.27 ± 0.10	98.00 ± 0.50/O	-0.73 ± 0.51
TRa-18347	T-4554/#2	1982	81.84 ± 0.13	81.75 ± 0.17	0.09 ± 0.21	81.80 ± 0.11	78.70 ± 0.30/O	3.10 ± 0.32
TRa-18348	T-4518/#2	1982	94.52 ± 0.14	93.58 ± 0.14	0.94 ± 0.20	94.05 ± 0.10	94.00 ± 0.80/O	0.05 ± 0.81
				Average	0.02 ± 0.44			0.41 ± 1.69

about 10% of the most exposed material was removed. The  $\text{H}_2\text{O}_2$  and HCl solutions were then syphoned-off and the carbonate was kept wet to reduce adsorption of atmospheric  $\text{CO}_2$  (Schleicher et al. 1998). Approximately 15 mg of carbonate material was weighed before starting the treatments. The samples were not weighed afterwards as they were not completely dried before the release of  $\text{CO}_2$ , but the amount of  $\text{CO}_2$  is an indicator of how much material was lost in the cleaning process.  $\text{CO}_2$  was released from the leached material using both the  $\text{H}_3\text{PO}_4$  and EA methods. We compared the results without cleaning with those obtained after leaching with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) or hydrochloric acid (HCl). The cleaning with  $\text{H}_2\text{O}_2$  and HCl was done to samples already loaded in the EA boats (aluminum or silver respectively) or the glass ampoules to avoid losses in sample transfer.

The cleaning methods were checked using IAEA C2 material as well as a marble sample from a quarry on Thassos, Greece, as process blank (Table 2). Neither of these materials can perfectly represent the laboratory-produced carbonate powder, nonetheless they can help to determine contamination caused by the treatment methods selected and demonstrate the reproducibility. The marble has not been milled, and the fragments are larger than the powder of the archived carbonates. This will influence the effectiveness of the leaching methods. The IAEA C2 travertine material has been milled and resembles the carbonate powder more closely. However, it contains some organic compounds that might affect the chemical treatment and the measurement result. Both marble and IAEA C2 underwent the same treatments as the archived carbonate samples with four repetitions each.

## RESULTS AND DISCUSSION

The  $^{14}\text{C}$  concentrations of the archived samples, measured in duplicate, are listed in Table 1. The reliability of these measurements is supported by their duplication. The average difference in  $^{14}\text{C}$  concentration of  $\text{CO}_2$  obtained by EA combustion and with  $\text{H}_3\text{PO}_4$  or by two EA combustions does not differ statistically from zero. The standard deviation of these differences, calculated from their scatter, agrees statistically with the measurement uncertainty calculated from the individual differences, provided two values (TRa-16393 (L-22-B), TRa-16395 (L-24),  $\text{H}_3\text{PO}_4$ ) are ignored. These two measurements show a significantly lower  $^{14}\text{C}$  content than the other measurements of the same samples (Tables 1 and 3). For TRa-16393 the difference from the measurement with EA combustion is  $-14.6$  pMC ( $41\sigma$ ) and for sample TRa-16395 it is  $-4.4$  pMC ( $16\sigma$ ). The results of these measurements do not match with any of the other samples treated at the same time so that we can exclude that the sample material was mixed up. We also exclude the possibility that the tools were not properly cleaned between handling samples because the difference is quite large and such a contamination would have been seen. While it is unclear what happened, we speculate that the most likely explanation is that some additional material has fallen into the sample glass between adding the sample and sealing the glass. However, such large variations have never been seen when measuring secondary standards. Both results were excluded from further analysis.

We tried to remove contamination by gentle leaching with  $\text{H}_2\text{O}_2$  and HCl solutions followed by extraction of  $\text{CO}_2$  in our Elemental Analyzer (EA) and with  $\text{H}_3\text{PO}_4$ , which resulted in four data sets. The Thassos marble blank and IAEA-C2 were used to check contamination introduced in this procedure. While the leaching with  $\text{H}_2\text{O}_2$  and HCl seems to have little effect on the blank value for  $\text{H}_3\text{PO}_4$  extraction, it causes an increase in  $^{14}\text{C}$  for the EA combusted samples (Table 2). The  $^{14}\text{C}$  concentrations measured for untreated material by EA combustion are about 0.15 pMC higher than for  $\text{CO}_2$  released by  $\text{H}_3\text{PO}_4$ , possibly due to a low organic

Table 2  $^{14}\text{C}$  content in pMC of process blanks (Thassos marble) and secondary standards (IAEA C2) according to  $\text{CO}_2$  extraction and cleaning methods. Symbol † indicates a measurement not used in the calculations.

No cleaning		$\text{H}_2\text{O}_2$ cleaning		HCl cleaning	
EA	$\text{H}_3\text{PO}_4$	EA	$\text{H}_3\text{PO}_4$	EA	$\text{H}_3\text{PO}_4$
<b>TRa-10149 Thassos marble</b>					
$0.286 \pm 0.007$	$0.075 \pm 0.004$	$0.905 \pm 0.016$	$0.125 \pm 0.007$	$0.993 \pm 0.012$	$0.074 \pm 0.004$
$0.256 \pm 0.008$	$0.091 \pm 0.007$	$0.462 \pm 0.013$	$0.062 \pm 0.003$	$1.142 \pm 0.014$	$0.070 \pm 0.005$
$0.214 \pm 0.006$	$0.087 \pm 0.004$	$0.263 \pm 0.008$	$0.165 \pm 0.005$	$0.443 \pm 0.009$	$0.065 \pm 0.004$
$0.184 \pm 0.005$	$0.075 \pm 0.004$	$5.398 \pm 0.031^\dagger$	$0.104 \pm 0.005$	$0.409 \pm 0.008$	$0.055 \pm 0.003$
Average					
$0.235 \pm 0.045$	$0.082 \pm 0.008$	$0.543 \pm 0.329$	$0.114 \pm 0.043$	$0.747 \pm 0.376$	$0.066 \pm 0.008$
<b>TRa-10138 IAEA C2 - 41.14 pMC</b>					
$41.67 \pm 0.11$	$41.29 \pm 0.09$	$41.30 \pm 0.22$	$41.23 \pm 0.09$	$42.37 \pm 0.26$	$41.06 \pm 0.08$
$41.57 \pm 0.08$	$41.89 \pm 0.08$	$41.28 \pm 0.12$	$40.66 \pm 0.08$	$41.56 \pm 0.08$	$40.52 \pm 0.07$
$41.42 \pm 0.08$	$42.06 \pm 0.08$	$41.27 \pm 0.12$	$41.25 \pm 0.08$	$39.96 \pm 0.08$	$41.09 \pm 0.07$
$41.31 \pm 0.08$	$41.25 \pm 0.08$	$48.52 \pm 0.12^\dagger$	$41.09 \pm 0.08$	$41.43 \pm 0.08$	$41.10 \pm 0.07$
Average					
$41.49 \pm 0.16$	$41.62 \pm 0.41$	$41.28 \pm 0.02$	$41.06 \pm 0.28$	$41.33 \pm 1.00$	$40.94 \pm 0.28$

Table 3 <sup>14</sup>C content of carbonate samples prepared with different to CO<sub>2</sub> extraction and cleaning methods. The <sup>14</sup>C contents without cleaning are from Table 1. Symbol † indicates a measurement not used in the calculations. The uncertainty in the listed averages is based on the scatter of the listed differences and the number of samples.

Original laboratory number	No cleaning average (pMC)	H <sub>2</sub> O <sub>2</sub> cleaning				HCl cleaning				
		EA		H <sub>3</sub> PO <sub>4</sub>		EA		H <sub>3</sub> PO <sub>4</sub>		
		Result (pMC)	Difference to no cleaning (pMC)	Result (pMC)	Difference to no cleaning (pMC)	Result (pMC)	Difference to no cleaning (pMC)	Result (pMC)	Difference to no cleaning (pMC)	
<b>Atmospheric samples</b>										
TRa-16393	L-22-B	171.25 ± 0.30	171.04 ± 0.30	-0.21 ± 0.42	172.29 ± 0.24	1.04 ± 0.38	170.32 ± 0.35	-0.93 ± 0.46	171.96 ± 0.26	0.71 ± 0.40
TRa-16394	L-23-C	173.77 ± 0.13	172.55 ± 0.29	-1.22 ± 0.32	173.51 ± 0.21	-0.26 ± 0.25	173.26 ± 0.33	-0.51 ± 0.35	174.01 ± 0.25	0.24 ± 0.28
TRa-16395	L-24	183.46 ± 0.18	184.50 ± 0.32	1.04 ± 0.37	184.90 ± 0.22	1.44 ± 0.28	183.08 ± 0.36	-0.38 ± 0.40	184.26 ± 0.16	0.80 ± 0.24
TRa-16396	L-25-B	184.53 ± 0.16	184.76 ± 0.33	0.23 ± 0.37	185.03 ± 0.25	0.50 ± 0.30	184.85 ± 0.37	0.32 ± 0.40	184.98 ± 0.23	0.45 ± 0.28
TRa-16397	L-26	184.54 ± 0.15	185.32 ± 0.35	0.78 ± 0.38	185.38 ± 0.20	0.84 ± 0.25	185.78 ± 0.43	1.24 ± 0.46	186.20 ± 0.27	1.66 ± 0.31
TRa-16398	L-27-B	188.03 ± 0.18	189.03 ± 0.37	1.00 ± 0.41	189.01 ± 0.17	0.98 ± 0.25	188.91 ± 0.37	0.88 ± 0.41	188.67 ± 0.20	0.64 ± 0.27
TRa-16399	L-28	186.27 ± 0.18	179.64 ± 0.31†	-6.63 ± 0.36†	186.15 ± 0.21	-0.12 ± 0.28	186.19 ± 0.40	-0.08 ± 0.44	186.14 ± 0.17	-0.13 ± 0.25
TRa-16400	L-29-B	181.91 ± 0.15	180.88 ± 0.31	-1.03 ± 0.34	182.10 ± 0.21	0.19 ± 0.26	182.00 ± 0.35	0.09 ± 0.38	181.90 ± 0.21	-0.01 ± 0.26
TRa-16401	L-358	128.25 ± 0.12	128.01 ± 0.17	-0.24 ± 0.21	128.55 ± 0.15	0.30 ± 0.19	128.70 ± 0.17	0.45 ± 0.21	128.96 ± 0.21	0.71 ± 0.24
TRa-16402	L-359	127.93 ± 0.11	127.69 ± 0.17	-0.24 ± 0.20	128.03 ± 0.21	0.10 ± 0.24	128.00 ± 0.18	0.07 ± 0.21	127.97 ± 0.17	0.04 ± 0.20
TRa-16403	L-360	128.48 ± 0.10	127.95 ± 0.18	-0.53 ± 0.21	128.27 ± 0.14	-0.21 ± 0.17	128.50 ± 0.20	0.02 ± 0.22	128.61 ± 0.16	0.13 ± 0.19
TRa-16404	L-361	127.74 ± 0.11	127.74 ± 0.17	0.00 ± 0.20	128.38 ± 0.22	0.64 ± 0.25	128.17 ± 0.18	0.43 ± 0.21	128.30 ± 0.14	0.56 ± 0.18
			Average	-0.04 ± 0.23	Average	0.45 ± 0.16	Average	0.13 ± 0.17	Average	0.48 ± 0.14
<b>Archaeological samples</b>										
TRa-16405	T-363	67.42 ± 0.07	67.22 ± 0.15	-0.20 ± 0.17	67.31 ± 0.13	-0.11 ± 0.15	67.02 ± 0.16	-0.40 ± 0.17	67.21 ± 0.11	-0.21 ± 0.13
TRa-16406	T-597	41.97 ± 0.06	41.56 ± 0.09	-0.41 ± 0.11	41.91 ± 0.16	-0.06 ± 0.17	41.32 ± 0.23	-0.65 ± 0.24	41.78 ± 0.07	-0.19 ± 0.09
TRa-16408	T-1031	59.77 ± 0.07	60.89 ± 0.16	1.12 ± 0.17	59.80 ± 0.10	0.03 ± 0.12	59.70 ± 0.18	-0.07 ± 0.19	59.42 ± 0.12	-0.35 ± 0.14
TRa-16409	T-4949A	64.52 ± 0.09	65.69 ± 0.20	1.17 ± 0.22	64.61 ± 0.10	0.09 ± 0.13	64.20 ± 0.17	-0.32 ± 0.19	64.82 ± 0.12	0.30 ± 0.15
TRa-16410	T-5099A	49.20 ± 0.07	54.51 ± 0.18†	5.31 ± 0.19†	49.37 ± 0.08	0.17 ± 0.11	48.96 ± 0.22	-0.24 ± 0.23	49.36 ± 0.08	0.16 ± 0.11
TRa-16411	T-5100A	33.69 ± 0.05	39.52 ± 0.22†	5.83 ± 0.23†	33.77 ± 0.07	0.08 ± 0.09	33.67 ± 0.26	-0.02 ± 0.26	33.88 ± 0.07	0.19 ± 0.09
TRa-16412	T-5130	43.89 ± 0.08	52.52 ± 0.18†	8.63 ± 0.20†	44.03 ± 0.08	0.14 ± 0.11	43.72 ± 0.23	-0.17 ± 0.24	44.08 ± 0.08	0.19 ± 0.11
			Average	0.42 ± 0.42	Average	0.05 ± 0.04	Average	-0.27 ± 0.08	Average	0.01 ± 0.10

contamination. One measurement of the Thassos marble blank with  $\text{H}_2\text{O}_2$  cleaning and EA combustion yielded a value of  $5.40 \pm 0.03$  pMC, approximately 10 times higher than the others. This measurement was considered an outlier and has not been included in the mean blank value for its method. A similar contamination was seen on a measurement of the IAEA-C2 samples at  $48.52 \pm 0.12$  pMC and for some of the unknowns (TRa-16399, TRa-16410-12, Table 3). The contamination offsets are different for each of the samples, but they are always directed towards the atmospheric  $^{14}\text{C}$  ratio at the time of preparation ( $\approx 101$  pMC). This leads to the conclusion that a modern contamination occurred during the leaching-EA treatment. It has been reported that carbonates are prone to uptake of atmospheric carbon after leaching with  $\text{H}_2\text{O}_2$  and also that keeping the samples wet afterwards prevents this effect (Schleicher et al. 1998). While we attempted to keep the samples wet while exposed to atmosphere, this could not be guaranteed when transferring the samples into the EA. The degree of drying would be different for each sample, explaining the different offsets that we observed. Meanwhile, keeping the samples wet and sealed from the atmosphere in the  $\text{H}_3\text{PO}_4$ - $\text{CO}_2$  extraction is not an issue. Accordingly, none of those results show an offset. While the specific measurements mentioned above were affected strongly by this issue, it cannot be excluded that other samples have been affected on a smaller scale. The results of the HCl-cleaned samples with EA treatment, show a larger scatter than the other methods, both for the IAEA-C2 and the marble samples (Table 2). In case of the C2 sample, the standard deviation is 1.0 pMC while it is only 0.16–0.41 pMC for the other methods. This could indicate that a similar adsorption effect also happened to some of these samples. The measurements with  $\text{CO}_2$  released by  $\text{H}_3\text{PO}_4$ , do not show such variations which is consistent with them being kept in vacuum after leaching.

The mean results of the Thassos marble samples (Table 2) were used for the process blank correction for archive samples subjected to the corresponding leaching methods.

For the testing of 49 archived samples, a total of 178 individual targets were measured in 16 different wheels together with a total of 160 reference samples (OXII) (Mann 1983) for normalization. The measurement uncertainty was verified with a  $\chi^2$  test of the OXII results (Turnbull et al. 2015). The mean uncertainty for the measurements, based on counting statistics, is 0.17 pMC and only a contribution of 0.07 pMC is needed to bring the observed scatter into statistical  $\chi^2$  agreement.

In addition to the measurement uncertainty and the method uncertainty determined by the IAEA-C2 measurements (0.13 pMC), an uncertainty of 0.4 pMC needs to be added to the individual measurements for statistical agreement in a  $\chi^2$  test, which would be attributed to inhomogeneity of the archived material itself. While a precision of 0.4 pMC would still be an improvement for the measurements of the archaeological samples, the required precision for relevant atmospheric measurements is 0.3% (Crotwell et al. 2019) which was not achieved with the measurement of the archived carbonates. The original measurements by gas proportional counting on large samples of fresh material had uncertainties of 0.5–1.2 pMC so that the variations we observed would not have been seen or present.

To assess sample homogeneity, L-22-B was sampled three times and each sub-sample was measured twice. The top layer was measured at  $171.57 \pm 0.19$  and  $170.95 \pm 0.30$  pMC, the middle layer at  $171.74 \pm 0.23$  and  $170.79 \pm 0.25$  pMC, and the lower layer at  $173.49 \pm 0.18$  and  $172.06 \pm 0.27$  pMC. While the top and middle aliquots statistically have the same values, the bottom one has a slightly higher  $^{14}\text{C}$  content. This difference indicates that the contamination that we observed may have been introduced from the top. All three layers are significantly

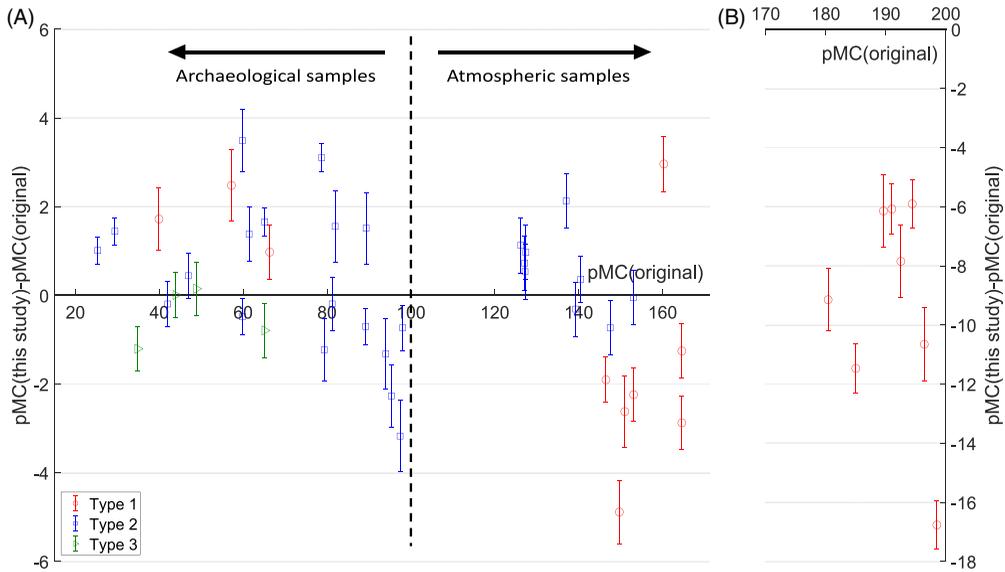


Figure 3 Deviation of measurement results from original value of  $^{14}\text{C}$  concentration (pMC) for uncleaned samples in different container types. (A) Archaeological samples and atmospheric samples from 1967 and later. (B) Atmospheric samples from 1963.

below the originally measured value of sample L-22 ( $180.4 \pm 1.0$  pMC) indicating that the contamination has considerable effect on all the material in the container.

To assess whether remeasurements of the archived atmospheric  $\text{CO}_2$  samples make sense, we have to confirm that the measurement results will accurately represent the atmosphere at the time of sampling. The atmospheric samples of 1963 show  $^{14}\text{C}$  concentration values that are significantly lower (6.0–16.8 pMC) than the original measurements by Nydal (Table 1, Figure 3B). Results for later atmospheric samples from 1967 to 1980 have to be compared to the datasets of Vermunt or Schauinsland as there are no original Nydal measurements (Table 1; Figure 3A). The difference is large for the samples in type 1 containers (L-187, 188, 226, 236, 238, 259) that are measured lower by 1.3–4.9 pMC. An exception is the result for L-189 from 1967-09-04 that is  $2.90 \pm 0.62$  pMC ( $4.7\sigma$ ) higher than its Vermunt counterpart. The explanation may be that this Vermunt  $^{14}\text{C}$  value is 4.3 pMC lower than that of the preceding samples 1967-08-07 and 1967-08-21 while our measured  $^{14}\text{C}$  value is quite similar to what we measured for the two preceding samples. This shift towards atmospheric values is corroborated by the  $^{14}\text{C}$ -depleted archaeological samples where samples in type 1 containers are all measured above the original values (1.1–2.5 pMC).

Seven atmospheric samples stored in type 2 containers (L-232, 252, 284, 285, 358-360) are in general statistical agreement with the corresponding reference datasets from Vermunt and Schauinsland (Levin and Kromer 2004). Two of the samples (L-286 and L-361 from December 1974 and November 1980, respectively) are more than  $3\sigma$  higher in  $^{14}\text{C}$  concentration than their reference values, which would not be expected from a contamination by later atmospheric  $\text{CO}_2$ . Since there are no original measurements for these samples, the comparison is with samples from a different location with, possibly, different local effects. For the Schauinsland record,  $^{14}\text{C}$  concentrations below clean-air at the Jungfrauoch by 2–6‰ in summer and 10–15‰ in winter

have been reported (Levin and Kromer 2004). This could explain that the archive measurements are higher in  $^{14}\text{C}$  than the Schauinsland and Vermunt records if the sampling location at Lindesnes reflects clean air during the sampling period. This is supported by measurements from Mace Head on the West coast of Ireland that show no significant difference in  $^{14}\text{C}$  concentration with the Jungfrauoch measurements (Levin and Kromer 2004) and by the location of Lindesnes that is also on the West coast, although facing the North Sea instead of the Atlantic Ocean. However, without an independent method of verification, we cannot validate this assumption, especially for the sampling period in question. Therefore, we cannot determine whether these samples in type 2 containers are uncontaminated. We therefore remeasured several archaeological samples archived in type 2 containers.

Eight out of 18 archaeological samples in type 2 containers differ by more than  $2\sigma$  (Table 1). This non-statistical behavior indicates individual contamination. Six remeasured samples show higher  $^{14}\text{C}$  concentrations, as expected for atmospheric contamination, with an average offset of  $2.03 \pm 0.41$  pMC. Two samples with  $97.40 \pm 0.80$  and  $95.30 \pm 0.70$  pMC were remeasured lower by  $3.15 \pm 0.81$  and  $2.25 \pm 0.71$  pMC, respectively. These off-sets are large compared with the  $\approx 0.8$  pMC uncertainty of the original measurement and the 0.4 pMC scatter discussed above. The results indicate that also the type 2 containers are unreliable to prevent atmospheric contamination during storage. This must also apply to the atmospheric samples from the Trondheim archive so that remeasurements may not provide  $^{14}\text{C}$  concentrations representative for the atmosphere at the time of sampling.

Only the type 3 containers seem to perform better with no indication of atmospheric contamination, but these were unfortunately not used for atmospheric samples.

We see that the difference between original and remeasurement is varying more than the uncertainties predict, even after considering additional uncertainty for inhomogeneity of the samples as described above. This means that the amount of contamination is varying individually for each sample and therefore cannot be corrected for by calculation. A crucial question is thus whether the contamination can reliably be removed. We tested “cleaning” the archived samples using established leaching protocols for carbonate samples.

Table 3 lists the  $^{14}\text{C}$  concentrations of the 12 atmospheric and 7 archaeological archive samples, cleaned with  $\text{H}_2\text{O}_2$  or  $\text{HCl}$ , and their  $\text{CO}_2$  prepared with EA or  $\text{H}_3\text{PO}_4$ . We compared these with their mean  $^{14}\text{C}$  values without cleaning from Table 1 and calculated the average change for each of the four methods. A removal of a modern contamination would affect the bomb- $^{14}\text{C}$ -enriched atmospheric and the  $^{14}\text{C}$ -decay-depleted archaeological samples in an antithetic way so that we split the evaluation for these groups. Outliers of the  $\text{H}_2\text{O}_2$ -EA treatment mentioned above are not used in the averages and are marked with † in the tables.

The strongest effect of the cleaning can be seen in the leaching methods combined with  $\text{H}_3\text{PO}_4$  extraction of  $\text{CO}_2$  for the atmospheric samples. The increase of  $0.45 \pm 0.16$  and  $0.48 \pm 0.14$  pMC in  $^{14}\text{C}$  concentration for  $\text{H}_2\text{O}_2$  and  $\text{HCl}$  leaching, respectively, documents a statistically significant, average removal of recent contamination. Significant also is that for  $\text{H}_2\text{O}_2$ , as 9 of 12 cleaned samples showed higher  $^{14}\text{C}$  values, 5 of which  $>2\sigma$ , and only 3 lower, but  $<2\sigma$ .  $\text{HCl}$  leaching gave similar improvements with 5  $^{14}\text{C}$  increases  $>2\sigma$  and 5  $<2\sigma$ , and only 2 decreases  $<2\sigma$  (Table 3). The increase of the measured  $^{14}\text{C}$  content indicates that part of the contamination is removed, and the results are more representative than for the uncleaned samples. The observed change is, unfortunately, still quite small, with a maximum of 1.66 pMC, compared to the differences from the original values of up to 16.8 pMC. Furthermore,

these cleaning methods seem to have no effect on the archaeological samples so that we cannot conclude that the cleaning produces reliable results.

The leaching methods combined with the EA combustions do not show, on average, a statistically significant change in  $^{14}\text{C}$  concentration for the atmospheric samples. The scatter in  $^{14}\text{C}$  changes is, however, large with three increases and three decreases  $>2\sigma$  for  $\text{H}_2\text{O}_2$  and four increases with one decrease  $>2\sigma$  for HCl. Considering the  $^{14}\text{C}$  increase for archaeological samples after  $\text{H}_2\text{O}_2$  leaching, we conclude that these samples were also subject to adsorption of atmospheric  $\text{CO}_2$  when drying after the leaching, although on a smaller level than the ones mentioned earlier. This seems to be less of an issue for the HCl leaching as the archaeological samples are measured on average 0.27 pMC lower after the leaching, which again corresponds to a limited removal of modern contamination. This corresponds to our expectations of modern contamination being removed, while adsorption of modern  $\text{CO}_2$  during EA-loading is small for these samples. However, we cannot explain why this would not have been observed for the HCl leaching in combination with  $\text{H}_3\text{PO}_4$ , other than that this is caused by the small number of samples measured.

The  $^{14}\text{C}$  concentrations for  $\text{CO}_2$  prepared with leaching and  $\text{H}_3\text{PO}_4$ , where we did not have adsorption of atmospheric  $\text{CO}_2$  during the treatment (Tables 2 and 3), show that the contamination evident in Table 1 was not completely removed by our  $\text{H}_2\text{O}_2$  and HCl leaching. Instead, we only removed about 10%. Leaching, which can successfully be applied to other sample types e.g., foraminifera (Schleicher et al. 1998), apparently is not effective in cleaning the finely powdered  $\text{CaCO}_3$  precipitate of the archived samples, probably because the surface to volume ratio is so high that contamination could affect every part of the sample.

## CONCLUSION

Archived carbonate samples of the Trondheim latitudinal network of atmospheric  $^{14}\text{C}$  sampling stations, started in 1962, show serious contamination, probably with atmospheric  $\text{CO}_2$ , which could not be removed by the chemical leaching methods applied in this study. Contamination is especially serious for the early samples from the 1960s that were stored in glass containers with a hard-plastic screw cap (type 1). Samples after 1971, largely stored in containers with a flexible squeeze-on plastic lid (type 2), show a variable, lower contamination.

The increased uncertainty in  $^{14}\text{C}$  concentration, due to a variable atmospheric contamination, negates benefits in precision that AMS could offer for these samples of atmospheric  $\text{CO}_2$ . Since the precise degree of contamination for an individual sample cannot be assessed, the archived samples are, unfortunately, no longer reliable to be of use in atmospheric datasets.

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