

## A $^{14}\text{C}$ CALIBRATION WITH AMS FROM 3500 TO 3000 BC, DERIVED FROM A NEW HIGH-ELEVATION STONE-PINE TREE-RING CHRONOLOGY

Franz Dellinger<sup>1</sup> • Walter Kutschera<sup>1,2</sup> • Kurt Nicolussi<sup>3</sup> • Peter Schieβling<sup>3</sup> Peter Steier<sup>1</sup> • Eva Maria Wild<sup>1</sup>

**ABSTRACT.** High-precision radiocarbon accelerator mass spectrometry (AMS) measurements of a new high-altitude stone-pine tree-ring chronology from the European Alps were performed for a 500-yr stretch in the second half of the 4th millennium BC. A  $^{14}\text{C}$  calibration curve with a typical 1- $\sigma$  uncertainty of about 20  $^{14}\text{C}$  yr was achieved. Although the general agreement of our data set with INTCAL98 is very good (confirming once more that INTCAL98 is also proper for calibration of samples of extraordinary sites), we found small deviations of  $17 \pm 5$   $^{14}\text{C}$  yr, indicating possible seasonal effects of the delayed growing season at high altitude.

### INTRODUCTION

It is well known that  $^{14}\text{C}$  calibration with tree rings is an indispensable prerequisite for accurate radiocarbon dating. It provides the absolute time reference for  $^{14}\text{C}$  content in the atmosphere during the past 12,000 yr. Although the global uniformity of  $^{14}\text{C}/^{12}\text{C}$  isotope ratios in atmospheric  $\text{CO}_2$  is a well-established fact, small deviations from the INTCAL98 calibration curve (Stuiver et al. 1998) have been recently reported (Kromer et al. 2001; Manning et al. 2001; Reimer 2001). In a steep section of the calibration curve between 850 BC and 750 BC, a shift of  $\sim 30$  yr was obtained by comparing INTCAL98 with a  $^{14}\text{C}$  calibration based on a (floating) tree-ring sequence of junipers from Anatolia, Turkey (*Juniperus excelsa* and *Juniperus foetidissima*). Kromer et al. (2001) pointed out that this small shift may have been caused by a regional  $^{14}\text{CO}_2$  offset linked to the different growing season of junipers as compared to German and Irish oaks used for INTCAL98.

In the present work, we performed high-precision  $^{14}\text{C}$  AMS measurements for a new high-altitude tree-ring chronology of stone pines (*Pinus cembra L.*) (Nicolussi and Schieβling 2001, 2002). Stone pines are the typical trees one finds at the timberline in the central parts of the European Alps (Figure 1). Our measurements covered the time period from 3500 BC to 3000 BC. On one hand, this time period is interesting since it includes the famous Iceman “Ötzi,” who lived around 3200 BC in the same Alpine region where the stone pines were collected. On the other hand, the calibration curve has similar steep sections as the juniper curve mentioned above, and a different growing season of the stone pines, as compared to the low-altitude German and Irish oaks of INTCAL98, suggest another possible observation of a regional  $^{14}\text{CO}_2$  offset. A prerequisite for such a comparison is a precision of  $^{14}\text{C}$  AMS measurements comparable to beta counting. How this could be accomplished at VERA is described separately (Steier et al., these proceedings).

### THE STONE-PINE TREE-RING CHRONOLOGY

The basis for our investigations was the new high-elevation stone-pine (*Pinus cembra L.*) tree-ring chronology established at the Institute of High Mountain Research of the University of Innsbruck (Nicolussi and Schieβling 2001, 2002). Until recently, absolutely dated multi-millennial chronologies (such as those existing for German and Irish oaks) did not exist in the Alps. The stone-pine

<sup>1</sup>Vienna Environmental Research Accelerator (VERA), Institut für Isotopenforschung und Kernphysik, Universität Wien, Währingerstrasse 17, A-1090 Wien, Austria.

<sup>2</sup>Corresponding author. Email: walter.kutschera@univie.ac.at.

<sup>3</sup>Institut für Hochgebirgsforschung, Universität Innsbruck, Innrain 52, A-6020 Innsbruck, Austria.



Figure 1 Fully-grown stone pine (*Pinus cembra L.*) near the timberline in the European Alps. (Photo courtesy of W Kutschera, 2003). As seen in this picture, the tree literally grows on a rock, hence the term “stone” pine seems appropriate.

chronology can be used as the dating base for the establishment of Alpine event records (e.g. Holocene glacier fluctuations, avalanche activity) and the reconstruction of summer temperatures (Nicolussi and Schießling 2001), respectively. In the Alps, there is always enough precipitation at timberline sites, and the main limiting factor for tree growth is the summer temperature. Therefore, from the tree-ring-width pattern, the information of the summer temperatures can be extracted.

In the course of several years, about a hundred subfossil logs were collected near the timberline, above 1900 m above sea level (asl). The logs came from 26 sites in the Hohe Tauern, Stubaier Alps, Zillertaler Alps, Ötztaler Alps, and in the Ortler Group. These collecting sites are in the general vicinity of the location where the famous prehistoric Iceman Ötzi was found (Kutschera et al. 2003). Stone pines were collected almost exclusively; the number of spruce (*Picea abies*) was only about 1% of the whole data set.

A continuous chronology was established ranging back more than 7000 yr, from the present day until 5125 BC (Figure 2). The mean replication of this continuous part is approximately 20, although some weaker replicated sections also exist. Including 3 other (floating) sections, the Alpine conifer tree-ring chronologies now cover nearly the entire Holocene (Figure 2).

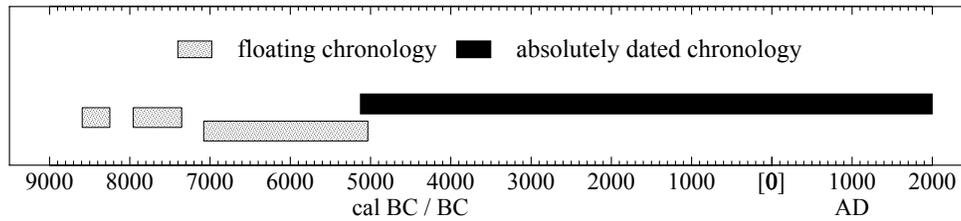


Figure 2 Current state of the central Eastern Alpine tree-ring chronologies. The absolutely dated continuous stone-pine chronology is about 7100 yr long and extends back to 5125 BC. It is based on approximately 430 sub-fossil logs and also includes more than 300 tree-ring series of living trees and sub-recent logs, respectively, in the latest section. The temporal positions of the floating chronologies have been assessed by wiggle-matching of <sup>14</sup>C dates. These 3 chronologies are based on about 50 subfossil logs of the species *Pinus cembra* (stone pine), *Larix decidua* (European larch), and *Picea abies* (Norway spruce).

### SAMPLE EXTRACTION, PREPARATION, AND PRETREATMENT

All trunks investigated in the present work originated from sites between 2150 and 2300 m asl (Table 1). The samples were selected at the Institute for High Mountain Research from the inside of the logs (far away from exposed surfaces). Water was used as a contrast amplifier for tree-ring counting, instead of the usual chalk to exclude possible contamination. For each sample, several cubic cm of wood were cut out and sent to the VERA Laboratory. For safe storage, the samples were first vacuum-dried at 60 °C overnight. The dry mass was between 0.6 and 1.4 g. For proper comparison with the INTCAL98 data set (Stuiver et al. 1998), which is given in decadal steps, we used 50 decadal tree-ring sections beginning with 3499–3490 BC until 3009–3000 BC.

Table 1 Characterization of the tree-ring samples from stone pines used in this work.

Tree log identifier	Collection site	Site coordinates	Elevation (m asl)	Tree rings (n)	Tree-ring period (yr BC)	Ring-width range (mm)	Decadal sections used
KRO-2	Krottenlacke Windachtal/Stubaier	46°57'15"N 11°06'05"E	2278	118	3508–3391	0.715–2.103	9
SSM-84	Schwarzsteinmoor Zillertaler Alps	47°01'45"N 11°48'55"E	2150	134	3467–3334	0.136–2.501	6
EBA-47	Ebenalm Ötztaler Alps	47°01'15"N 10°57'55"E	2170	111	3351–3241	0.637–3.353	6
SSM-102	Schwarzsteinmoor Zillertaler Alps	47°01'45"N 11°48'55"E	2150	307	3312–3006	0.124–0.958	10
EBA-46	Ebenalm Ötztaler Alps	47°01'15"N 10°57'55"E	2170	172	3211–3040	0.314–2.733	9
GDM-40	Daunmoränensee Kaunertal/Ötztaler Alps	46°53'40"N 10°43'30"E	2295	355	3188–2834	0.416–1.553	10

From each sample material, a 1-mm-thick slice was cut from the trunk axis by using a fretsaw. The (usually oiled) saw blades were washed in acetone in an ultra-sonic bath for 10 min and then heated for 1 hr at 550 °C in the furnace. A stick of wood was then cut out with a scalpel for tree rings covering exactly 10 yr. A thickness of 1 to 2 mm was chosen so that the mass of the wood stick was slightly above 10 mg (see Figure 3). In this step, care was taken that the chosen wood stick did not contain any visible resin channels.

Our standard acid-base-acid procedure was used for sample pretreatment (1M HCl at 60 °C for 1 hr, 0.1 M NaOH at 60 °C for 1 hr, 1M HCl at 60 °C for 1 hr). Typically, this procedure resulted in a loss of sample weight of a few percent. The good state of preservation of the sample was indicated by the fact that very little humic acids were visible. The pretreated samples were vacuum-dried overnight.

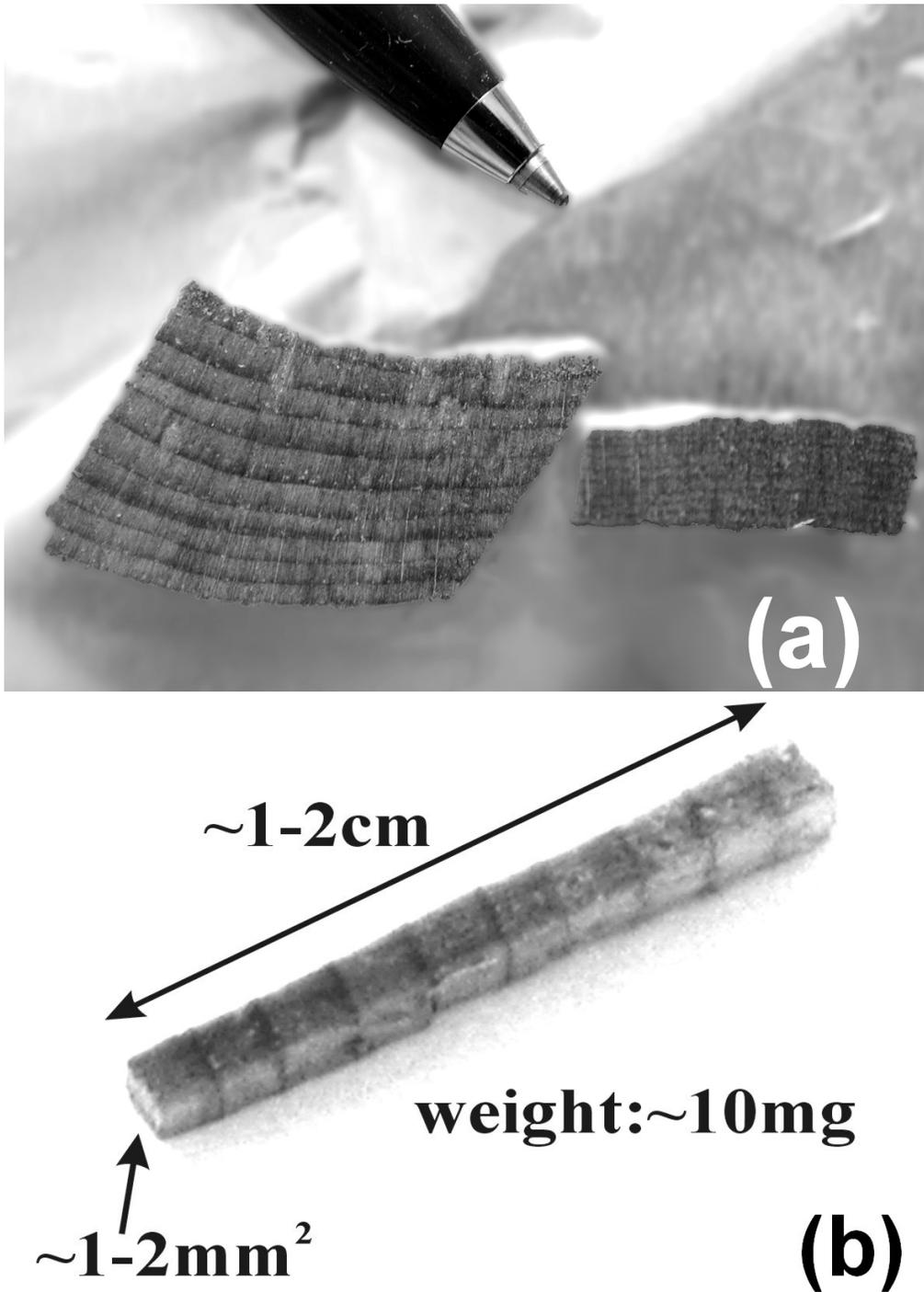


Figure 3 Typical decadal wood samples: (a) 2 pieces of wood with different tree ring widths, from which sticks shown in (b) were cut for sample preparation. The sticks were converted into graphite samples for the AMS measurement. The contribution of the various tree rings to the sample mass depends on the ring width.

The combustion of the sample material took place at 900 °C for 4 hr in a flame-sealed quartz tube containing 1g CuO as oxidant and some silver wire. The sample CO<sub>2</sub> was then reduced to elemental carbon at 610 °C using H<sub>2</sub> and an iron catalyst (Vogel et al. 1984). The mixture of graphite and catalyst was divided and pressed into 2 aluminium target holders suitable for our 40-position MC-SNICS ion source. Both sputter targets were measured.

### **AMS MEASUREMENTS**

The measurement of the stone-pine samples was performed in 5 separate AMS beam times (runs). Run 1 only contained material of the “KRO-2” tree slice, while in run 2, 3, and 4, material of all other tree slices was used. An additional run (run 5) was performed for samples which showed a deviation of more than 2  $\sigma$  from INTCAL98 in the preliminary evaluation of runs 1 to 4. Samples which got lost in chemical pretreatment were also measured in run 5.

In run 1, IAEA C-3 cellulose ( $129.41 \pm 0.06$  pMC) and IAEA C-5 wood ( $23.05 \pm 0.02$  pMC) were used as standard materials (Rozanski et al. 1992). It turned out to be advantageous to use wood of 10 tree rings (3239–3230 BC) of the dendro-dated FIRI-D wood as standard material instead of the C-5 wood in the remaining runs. The FIRI-D wood from the Fourth International Radiocarbon Inter-comparison (Scott 2003) has a higher pMC value ( $57.17 \pm 0.06$ ) and the wood chips of FIRI-D behave more similar to the actual samples than the powdered C-5 wood. For each run, 2 chemically independent standards were produced from FIRI-D wood and C-3 cellulose, respectively. For the standards, splits from the same graphite were exchanged between the runs to increase the diversity of standard material. After run 2, the idea arose to permute also the doublets of the samples with another wheel. Hence, we decided to mount single samples in the target wheel of run 3 and measure all the doublets in run 4.

Compared to routine measurements which usually take 24 hr, the stone-pine measurements lasted approximately 3 days per run. For such long measurement periods, it is necessary to retune the AMS facility once per day (Steier et al. 2004).

### **DATA EVALUATION AND RESULTS**

Each run is evaluated separately using the present version of the program “EVALGEN” (Puchegger et al. 2000), which is also used for routine measurements. For yet unknown reasons, the quality of the data varied for the different “tunings” of 1 run, judged from the reproducibility of the sample results and from the agreement of the standards with the nominal values. The evaluation program takes this into account by assigning additional uncertainties to the measured isotope ratios. So the final precision may even improve if data from such a tuning are left out. In some cases, the reason for the uncertainty can be identified and a workaround can be found. For example, the first tuning of run 5 could be used after normalizing to the low energy <sup>12</sup>C<sup>-</sup> current instead of the usual <sup>12</sup>C<sup>3+</sup> current. Obviously, the accelerator transmission of the <sup>12</sup>C<sup>-</sup> beam was not constant for this setup, but the <sup>13</sup>C and <sup>14</sup>C were not affected.

From 12 chemically independent ABA pretreatments of the standards, one was rejected as an outlier because all targets of this material showed a consistent deviation of  $\sim 50$  <sup>14</sup>C yr (which is more than 2  $\sigma$ ) in all 3 runs where this graphite was used. We think that contamination during the pretreatment is the most likely reason. Additionally, 1 single standard target was excluded in run 4. The same graphite in run 3 showed regular results. A possible reason for a deviation of 1 single target may be contamination during target pressing.

The exclusion of certain standards is no problem for measurement precision. At least 8 standards are mounted in each target wheel. Even if 2 standards are excluded (run 4), the 6 remaining are sufficient to calculate external uncertainties.

The final results of all stone-pine measurements are listed in Table 2. The dendro date in column 2 is the medium of the respective 10-yr tree-ring section. The  $^{14}\text{C}$  ages of run 3 and run 4 are combined by building the weighted mean treated as 1 measurement (run 3+4) in the following.

For most samples, a total 1- $\sigma$  uncertainty of less than 20  $^{14}\text{C}$  yr could be achieved, corresponding to an overall precision of 2.5‰ for the  $^{14}\text{C}$  determination. Compared to routine  $^{14}\text{C}$  measurements, this precision is mainly due to longer measurement times and the larger number of standards and their arrangement.

### DATA INTERPRETATION AND ANALYSIS

The overall agreement of the stone-pine measurements with INTCAL98 is very good (see Figure 4). However, by taking a closer look at the curve, small offsets in certain sections can be recognized. First, the whole data set of run 1 tends to be shifted to older  $^{14}\text{C}$  ages. Second, in the section of approximately 3410–3260 BC (i.e. the steep decline of the calibration curve), the data are shifted to younger  $^{14}\text{C}$  ages, independent from the measurement in which they were obtained. For the data of run 5, this trend to younger values remains for the calendar section 3260–3000 BC, while the data points of run 2 and run 3+4 are distributed almost equally to older and younger ages. Although these shifts can be clearly seen, they have to be carefully interpreted. Such offsets may come from systematic errors in the measurements and would then not be meaningful in terms of a paleoclimatic interpretation.

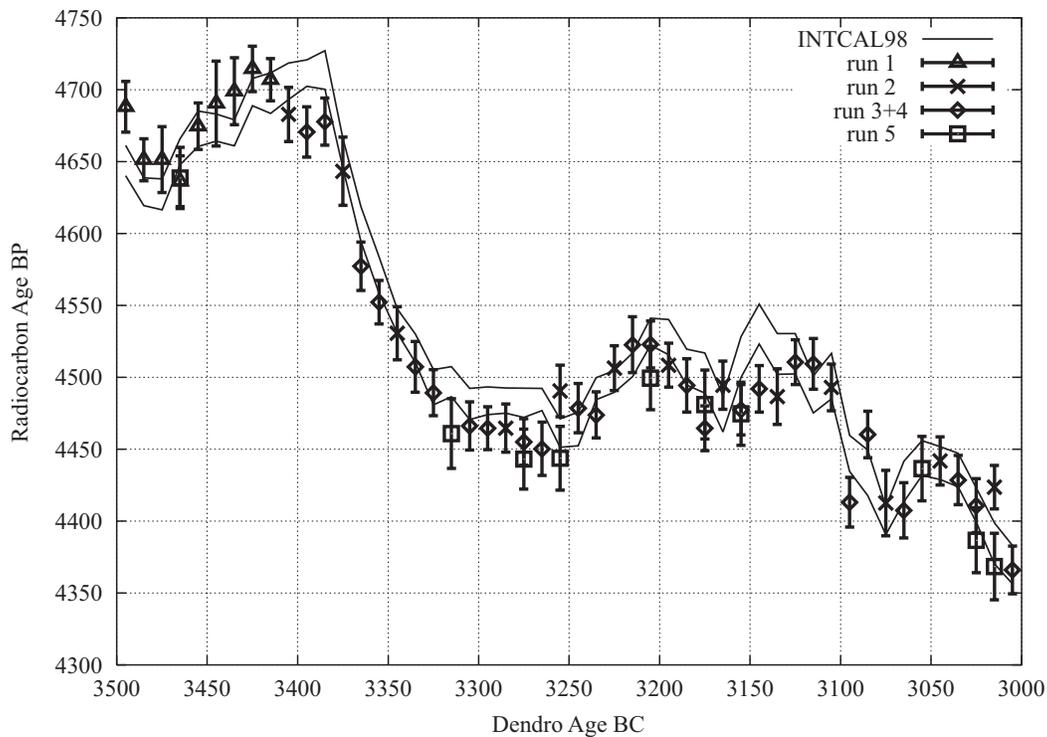


Figure 4 Comparison of the results from the present work (run 1, 2, 3+4, and 5) with the INTCAL98 calibration curve

Table 2 Comparison of the <sup>14</sup>C results for stone-pine samples with INTCAL 98.

Dendro data		VERA data				INTCAL 98
Tree log identifier	Date BC	VERA nr	Run #	δ <sup>13</sup> C (‰)	<sup>14</sup> C age (BP)	INTCAL 98 (BP)
KRO-2-1	3495	V2384/1	1	-18.7 ± 0.5	4688 ± 18	4650.7 ± 10.5
KRO-2-2	3485	V2385/1	1	-18.6 ± 0.6	4651 ± 15	4629.1 ± 9.6
KRO-2-3	3475	V2386/1	1	-18.3 ± 0.4	4651 ± 23	4627.2 ± 10.7
KRO-2-4	3465	V2387/1	1	-18.9 ± 0.6	4636 ± 18	4656.8 ± 9.0
KRO-2-4	3465	V2387/2	5	-22.2 ± 0.3	4639 ± 21	4656.8 ± 9.0
KRO-2-5	3455	V2388/1	1	-19.5 ± 0.5	4675 ± 16	4672.9 ± 12.3
KRO-2-6	3445	V2389/1	1	-18.7 ± 0.8	4690 ± 30	4673.7 ± 9.4
KRO-2-7	3435	V2390/1	1	-19.7 ± 1.1	4699 ± 23	4670.0 ± 9.0
KRO-2-8	3425	V2391/1	1	-18.2 ± 0.5	4714 ± 16	4698.4 ± 9.5
KRO-2-9	3415	V2392/1	1	-19.7 ± 0.6	4707 ± 15	4697.6 ± 14.1
SSM-84-1	3405	V2393/1	2	-19.8 ± 0.6	4683 ± 19	4705.8 ± 12.7
SSM-84-2	3395	V2394/1	3+4	-21.8 ± 0.4	4671 ± 18	4711.5 ± 9.2
SSM-84-3	3385	V2395/1	3+4	-22.2 ± 0.3	4678 ± 16	4713.7 ± 13.4
SSM-84-4	3375	V2396/1	2	-22.8 ± 1.0	4643 ± 24	4655.9 ± 10.2
SSM-84-5	3365	V2397/1	3+4	-21.2 ± 0.3	4577 ± 17	4606.4 ± 12.1
SSM-84-6	3355	V2398/1	3+4	-21.6 ± 0.3	4552 ± 15	4571.0 ± 12.6
EBA-47-1	3345	V2399/1	2	-22.7 ± 0.4	4531 ± 18	4539.3 ± 8.4
EBA-47-2	3335	V2400/1	3+4	-21.5 ± 0.3	4507 ± 18	4520.3 ± 9.9
EBA-47-3	3325	V2401/1	3+4	-22.1 ± 0.3	4489 ± 16	4493.1 ± 12.2
EBA-47-4	3315	V2402/1	5	-23.1 ± 0.2	4461 ± 24	4497.0 ± 10.5
EBA-47-5	3305	V2403/1	3+4	-23.0 ± 0.3	4466 ± 17	4481.4 ± 10.8
EBA-47-6	3295	V2404/1	3+4	-22.6 ± 0.3	4465 ± 15	4483.7 ± 9.6
SSM-102-1	3285	V2405/1	2	-23.3 ± 0.2	4465 ± 17	4483.8 ± 8.7
SSM-102-2	3275	V2406/1	3+4	-20.8 ± 0.2	4455 ± 16	4482.2 ± 10.2
SSM-102-2	3275	V2406/2	5	-22.8 ± 0.4	4443 ± 21	4482.2 ± 10.2
SSM-102-3	3265	V2407/1	3+4	-23.4 ± 0.3	4450 ± 19	4484.6 ± 7.7
SSM-102-4	3255	V2408/1	2	-24.3 ± 0.3	4490 ± 18	4461.2 ± 9.9
SSM-102-4	3255	V2408/2	5	-24.7 ± 1.8	4444 ± 22	4461.2 ± 9.9
SSM-102-5	3245	V2409/1	3+4	-21.7 ± 0.3	4479 ± 17	4464.1 ± 11.7
SSM-102-6	3235	V2410/1	3+4	-22.0 ± 0.3	4474 ± 16	4492.1 ± 7.7
SSM-102-7	3225	V2411/1	2	-22.7 ± 0.2	4506 ± 16	4497.2 ± 7.6
SSM-102-8	3215	V2412/1	3+4	-21.2 ± 0.3	4523 ± 19	4508.7 ± 8.2
SSM-102-9	3205	V2413/1	3+4	-22.5 ± 0.3	4523 ± 16	4531.7 ± 9.5
SSM-102-9	3205	V2413/2	5	-22.4 ± 0.2	4499 ± 22	4531.7 ± 9.5
SSM-102-10	3195	V2414/1	2	-22.9 ± 0.5	4508 ± 15	4527.9 ± 12.2
EBA-46-1	3185	V2415/1	3+4	-23.5 ± 0.4	4494 ± 19	4507.1 ± 12.5
EBA-46-2	3175	V2416/1	3+4	-24.6 ± 0.3	4465 ± 16	4503.0 ± 14.0
EBA-46-2	3175	V2416/2	5	-25.5 ± 0.8	4481 ± 24	4503.0 ± 14.0
EBA-46-3	3165	V2417/1	2	-26.1 ± 0.8	4495 ± 19	4474.7 ± 12.6
EBA-46-4	3155	V2418/1	3+4	-24.7 ± 0.3	4477 ± 18	4514.2 ± 14.1
EBA-46-4	3155	V2418/2	5	-24.4 ± 0.5	4475 ± 22	4514.2 ± 14.1
EBA-46-5	3145	V2419/1	3+4	-23.1 ± 0.3	4492 ± 16	4537.0 ± 13.9
EBA-46-6	3135	V2420/1	2	-25.3 ± 0.5	4487 ± 19	4516.3 ± 14.2
EBA-46-7	3125	V2421/1	3+4	-22.0 ± 0.3	4511 ± 16	4516.4 ± 14.1
EBA-46-8	3115	V2422/1	3+4	-24.0 ± 0.4	4509 ± 18	4488.1 ± 12.9
EBA-46-9	3105	V2423/1	2	-24.9 ± 0.4	4493 ± 16	4500.8 ± 15.8
GDM-40-1	3095	V2424/1	3+4	-22.9 ± 0.3	4413 ± 17	4447.1 ± 12.6
GDM-40-2	3085	V2425/1	3+4	-22.1 ± 0.3	4460 ± 16	4433.6 ± 15.8
GDM-40-3	3075	V2426/1	2	-24.6 ± 0.2	4413 ± 23	4400.4 ± 9.7
GDM-40-4	3065	V2427/1	3+4	-23.3 ± 0.3	4407 ± 19	4427.6 ± 14.1
GDM-40-5	3055	V2428/1	5	-23.6 ± 0.8	4437 ± 22	4443.9 ± 12.1
GDM-40-6	3045	V2429/1	2	-22.9 ± 0.2	4442 ± 17	4440.4 ± 11.4
GDM-40-7	3035	V2430/1	3+4	-24.1 ± 0.3	4429 ± 17	4435.5 ± 11.7
GDM-40-8	3025	V2431/1	3+4	-23.1 ± 0.4	4411 ± 19	4411.2 ± 12.0
GDM-40-8	3025	V2431/2	5	-23.6 ± 1.3	4387 ± 23	4411.2 ± 12.0
GDM-40-9	3015	V2432/1	2	-23.5 ± 0.2	4424 ± 15	4384.5 ± 14.2
GDM-40-9	3015	V2432/2	5	-22.2 ± 0.8	4368 ± 23	4384.5 ± 14.2
GDM-40-10	3005	V2433/1	3+4	-21.8 ± 0.3	4366 ± 17	4369.8 ± 13.3

In the statistical analysis, we wanted to investigate the significance of the deviations of the stone-pine data. In the first step, we calculated the difference between every stone-pine data point and the associated INTCAL98 data point. Subsequently, the mean deviation for every run was determined:  $+15.1$   $^{14}\text{C}$  yr for run 1,  $-0.7$   $^{14}\text{C}$  yr for run 2,  $-15.1$   $^{14}\text{C}$  yr for run 3+4, and  $-25.3$   $^{14}\text{C}$  yr for run 5. These offsets may originate in a systematic error which is correlated for all samples in a whole run. This error cannot be reduced by averaging and is the same for each individual sample and for the average of a complete measurement. However, this uncertainty cancels out if the average bias of a run is subtracted from the data points. In the corrected data, it can be explored if there are significant differences between the flat part of the calibration curve and the region with the steep decline. Unfortunately, the samples of run 1 cover only a short calendar period and not even 1 single data point lies in the steep part of the curve. As a consequence, these data could not be utilized in the calculations above.

In Figure 5, the deviation of the offset-corrected data points from the INTCAL98 curve are plotted. The error bars include the internal uncertainty of the stone-pine data points and the uncertainty of INTCAL98. The plot suggests that deviations from INTCAL98 may exist. For a statistical check, we divided the data set into 2 parts. The data points in the steep part between 3410 and 3260 BC generally seem to be located below the average, while in the flatter region from 3260 to 3000 BP, the deviation is slightly positive. The solid lines in the plot are the weighted mean values in the 2 regions. The mean values confirm the visual impression: the resulting difference of the 2 regions of  $16.6 \pm 4.8$  yr is statistically significant at  $3.4 \sigma$ .

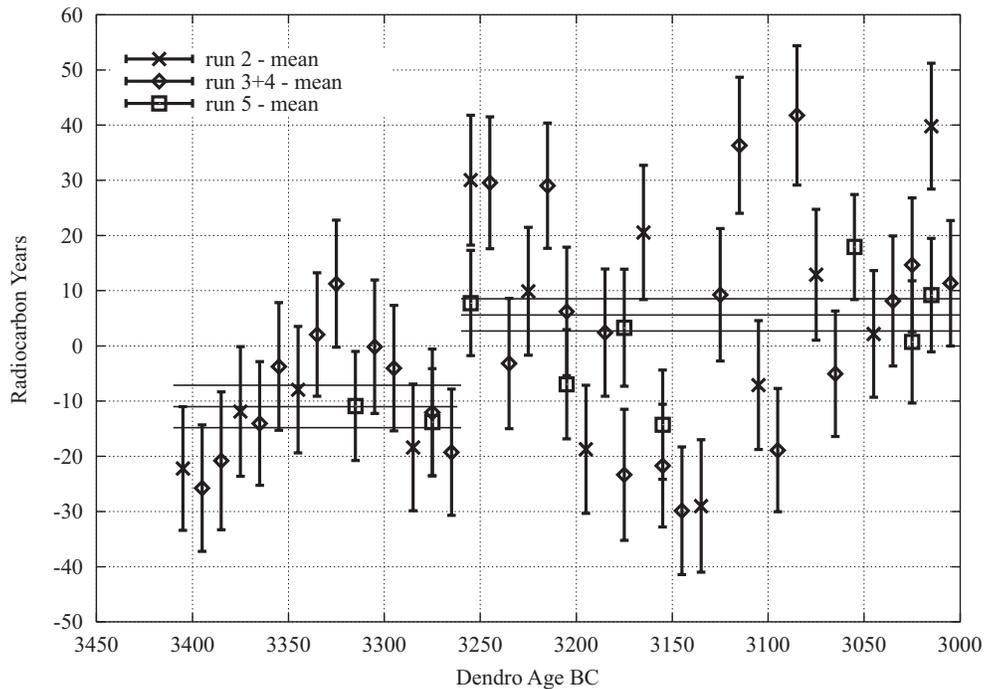


Figure 5 Difference between the  $^{14}\text{C}$  calibration from the stone pine and INTCAL98. For details of the procedure for how to arrive at the different offsets indicated by the horizontal lines ( $\pm 1 \sigma$ ), see text.

To investigate whether the uncertainties of the data points in each of the 2 regions are realistic, a  $\chi^2$  test was performed. For the region 3410–3260 BC consisting of 16 data points, a  $\chi^2$  of 5.86 was determined (25.0 is allowed for 95% confidence). Concerning the region 3260–3000 BC, the test resulted in a  $\chi^2$  of 39.1 (45.0 is allowed at 95% confidence for 32 data points).

**POSSIBLE EXPLANATION FOR THE SMALL SHIFT IN CALIBRATION**

Interestingly, similar deviations have been observed by Kromer et al. (2001) and Manning et al. (2001) in Turkish junipers. At a sharp drop of the calibration curve around 800 BC, the data of Turkish junipers were shifted by about 30 yr towards older <sup>14</sup>C ages relative to the (mainly) German oaks of INTCAL98. It is argued that the reason for this deviation lies in the seasonal variability of atmospheric <sup>14</sup>C. In Figure 6, our understanding of the emerging deviations based on the discussion in Kromer et al. (2001) is illustrated.

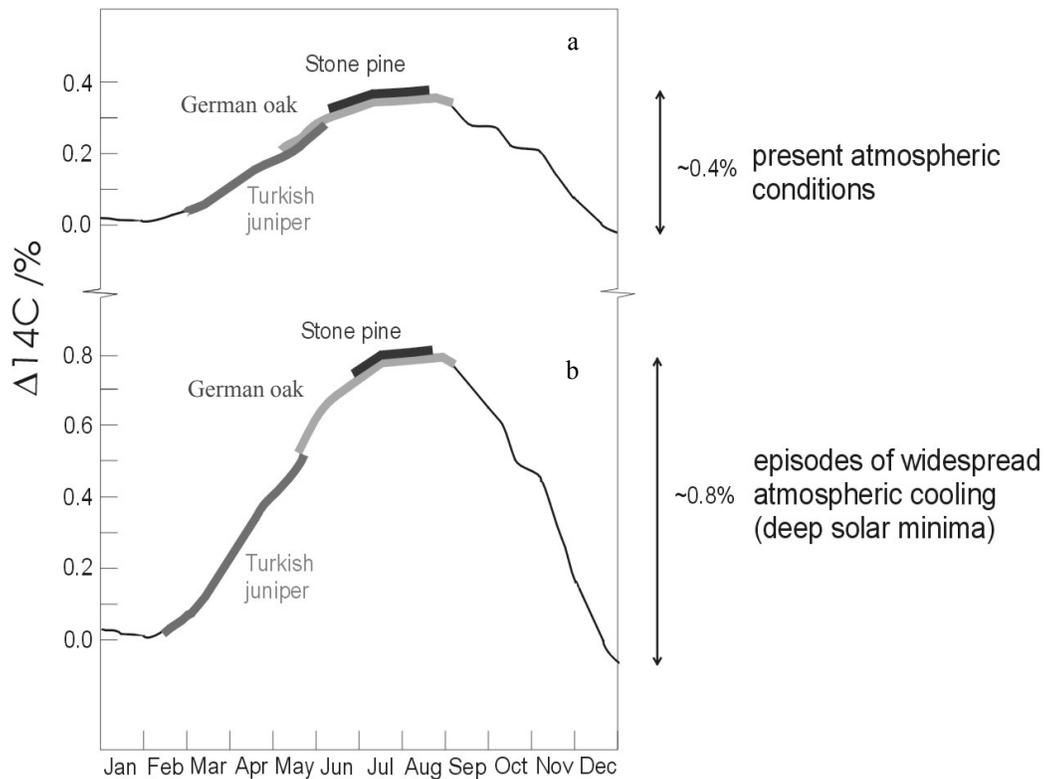


Figure 6 Our understanding of Kromer et al. (2001). The preindustrial/prebomb seasonal variability of <sup>14</sup>C is shown for atmospheric conditions similar to the present ones (a), and for deep solar minima which are also episodes of widespread atmospheric cooling (b). The different growth cycles of the various tree species is manifested in the  $\Delta^{14}\text{C}$ . In (b), the seasonal variability is larger and the colder climate causes later growth of the stone pine, whereas higher precipitation allows earlier growth of the Turkish juniper. This increases the differences between the 3 species.

From modeling bomb <sup>14</sup>C (Hesshaimer 1997) and from present-day tropospheric <sup>14</sup>C monitoring networks (Levin and Hesshaimer 2000), variations of 4‰ between low winter/spring and maximum summer activity have been deduced (Kromer et al. 2001). Depending on the rate of carbon uptake during the growing season and the phase relation of the growing seasons between the different

regions, different parts of this seasonal cycle are seen. Turkish junipers, for instance, start their main wood production earlier in spring than German oaks do. Hence, due to the intra-annual variations of the seasonal cycle, the wood of the Turkish junipers is depleted in  $^{14}\text{C}$  compared to the wood of German oaks. As the amplitude of the seasonal cycle is proportional to the  $^{14}\text{C}$  influx from the stratosphere, the effect of intra-annual variations should be best observable during times of “deep” solar minima. In these times, the amplitude of the seasonal cycle is supposed to be twice as large as in the average of the 11-yr solar cycle (Kromer et al. 2001; Masarik and Beer 1999). Such periods of enhanced  $^{14}\text{C}$  production appear as a steep decline in the calibration curve.

Following the previous argument, the stone pines should be higher in  $^{14}\text{C}$  than German oaks and appear younger due to the later growing season at high elevation sites. That agrees with the observed offset in our measurement.

## CONCLUSIONS

To our knowledge, this is the first high-altitude calibration curve which has been established by AMS. In our measurements, we achieved a typical 1- $\sigma$  uncertainty of about 20  $^{14}\text{C}$  yr (2.5‰) at a reasonable increase of effort. The results of the stone-pine measurements confirm once more that INTCAL98 is also proper for calibration of samples of extraordinary sites, such as the timberline in the Alps. Although the agreement of our data set with INTCAL98 is very good, at the edge of statistical analysis we found small deviations of  $17 \pm 5$   $^{14}\text{C}$  yr. Considering the argumentation of Kromer et al. (2001), this shift seems reasonable.

## REFERENCES

- Hesshaimer V. 1997. Tracing the global carbon cycle with bomb radiocarbon. [PhD dissertation]. Heidelberg: University of Heidelberg.
- Kromer B, Manning S, Kuniholm P, Newton M, Spurk M, Levin I. 2001. Regional  $^{14}\text{CO}_2$  offsets in the troposphere: magnitude, mechanism, and consequences. *Science* 294:2529–32.
- Kutschera W, Müller W. 2003. “Isotope language” of the Alpine Iceman investigated with AMS and MS. *Nuclear Instruments and Methods in Physics Research B* 204:705–19.
- Levin I, Hesshaimer V. 2000. Radiocarbon—a unique tracer of global carbon cycle dynamics. *Radiocarbon* 42(1):69–80.
- Manning S, Kromer B, Kuniholm P, Newton M. 2001. Anatolian tree rings and a new chronology for the East Mediterranean Bronze-Iron Ages. *Science* 294:2532–5.
- Masarik J, Beer J. 1999. Simulation of particle fluxes and cosmogenic nuclide production in the earth’s atmosphere. *Journal of Geophysical Research* 104D: 12,099–111.
- Nicolussi K, Schießling P. 2001. Establishing a multi-millennial *Pinus cembra* chronology for the central Eastern Alps, Conference “Tree Rings and People,” 22–26 September 2001, Davos, Switzerland. <http://www.wsl.ch/forest/dendro2001>.
- Nicolussi K, Schießling P. 2002. A 7000-year-long continuous tree-ring chronology from high-elevation sites in the central Eastern Alps. *Dendrochronology, Environmental Change and Human History*, Abstracts: 251–252, 6th International Conference on Dendrochronology, Quebec City, Canada, 22–27 August 2002.
- Puchegger S, Rom W, Steier P. 2000. Automated evaluation of  $^{14}\text{C}$  AMS measurements. *Nuclear Instruments and Methods in Physics Research B* 172:274–80.
- Reimer JR. 2001. A new twist in the radiocarbon tale. *Science* 294:2494–5.
- Rozanski K, Stichler W, Gonfiantini R, Scott EM, Beukens R, Kromer B, van der Plicht J. 1992. The IAEA  $^{14}\text{C}$  intercomparison exercise 1990. *Radiocarbon* 34(3):506–19.
- Scott EM. 2003. The Fourth International Radiocarbon Intercomparison (FIRI). *Radiocarbon* 45(2):135–291.
- Steier P, Dellinger F, Kutschera W, Rom W, Wild EM. 2004. Pushing the precision limit of  $^{14}\text{C}$  measurements with AMS. *Radiocarbon*, these proceedings.
- Stuiver M, Reimer PJ, Bard E, Beck JW, Burr GS, Hughen KA, Kromer B, McCormac G, van der Plicht J, Spurk M. 1998. INTCAL98 radiocarbon age calibration, 24,000–0 cal BP. *Radiocarbon* 40(3):1041–83.
- Vogel JS, Southon JR, Nelson DE, Brown T. 1984. Performance of catalytically condensed carbon for use in accelerator mass spectrometry. *Nuclear Instruments and Methods in Physics Research B* 5:289–93.