AMS $^{14}$C DATING OF EQUIPMENT FROM THE ICEMAN AND OF SPRUCE LOGS FROM THE PREHISTORIC SALT MINES OF HALLSTATT

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ABSTRACT. This paper summarizes radiocarbon measurements of mainly botanical samples from the Iceman (“Ötzi”) and from his discovery site, an Alpine glacier at the Austrian-Italian border. The results were obtained by accelerator mass spectrometry (AMS) at 3 different laboratories (Vienna, Austria; Uppsala, Sweden; Gif-sur-Yvette, France) between 1992 and 1997. All the dates, except 2, are consistent with the time period 3360–3100 BC, as previously determined from bone and tissue samples from the Iceman himself. The 2 exceptional dates from wooden artifacts suggest that the site of the Iceman was used as a mountain pass for millennia prior to and after the lifetime of “Ötzi”.

For a 2nd sample complex, we studied logs from the beginning of salt mining in the world’s oldest salt mines at Hallstatt in Upper Austria. $^{14}$C AMS measurements were performed in Vienna on spruce samples found in the prehistoric mines and from a log-house on the surface. Data evaluation included “wiggle matching” of different sets of tree rings. The results suggest that salt mining in the Hallstatt region took place in the 14th–13th century BC, well before the so-called Hallstatt period.

We discuss in some detail the chemical pretreatment of the samples and the data evaluation. We also present a comprehensive survey of $^{14}$C dates available in the literature concerning both botanical remains from the vicinity of the Iceman and from the earliest salt mining in Hallstatt.

INTRODUCTION

Recently, 2 sample complexes of considerable archaeological significance to the early history of the Central European region were radiocarbon dated at the Vienna Environmental Research Accelerator (VERA).

Equipment from the Iceman

On 19 September 1991, a mummified corpse was discovered accidentally by tourists at the “Tisenjoch”, a high Alpine mountain pass near the Italian–Austrian border (3120 m asl). The find was quickly nicknamed “The Iceman” or “Ötzi” (after the site location in the Ötztal Alps) and received widespread attention (see e.g. Coghlan 1992; Jaroff 1992; Bahn and Everett 1993; Roberts et al. 1993; Barfield 1994). $^{14}$C accelerator mass spectrometry (AMS) measurements performed on bone and on tissue samples (Bonani et al. 1992, 1994; Hedges et al. 1992; Prinoth-Fornwagner and Niklaus 1994) proved that the Iceman is world’s oldest known intact mummy. Many pieces of the Iceman’s equipment and other materials associated with his location were recovered in several post-excavations (Lippert 1992; Spindler 1993; Bagolini et al. 1995), taking place shortly after and during the cleansing of the mummy at the Römisch-Germanisches Zentralmuseum in Mainz, Germany (Egg 1992). However, only a very small fraction of these additional findings has been dated and published so far (Bonani et al. 1994; Prinoth-Fornwagner and Niklaus 1994). Botanical details of findings in connection with the Iceman are discussed in Bortenschlager et al. (1992) and Oeggl (1995). Here, we summarize the $^{14}$C dating measurements performed at 3 different AMS laboratories on a representative fraction of these mainly botanical samples (see also Kutschera et al. 1998).

Spruce Logs from the Prehistoric Salt Mines of Hallstatt

The salt mines of Hallstatt, the oldest in the world (Barth 1993; Lippert 1985), are probably the most important prehistoric industrial sites in Europe. They provided the basis for the enormous wealth of this region at that time. They lasted through 3 prehistoric periods (the (Late) Bronze Age, the Early Iron Age, and the period around 1 AD, respectively), which are topographically associated with the
so-called Northern, Eastern and Western mining groups (Schauberger 1960; Lippert 1985). Each of these groups had its distinct salt production technology (Urban 1989; Barth 1993). The importance of salt for this region is reflected in the syllable “Hall”, which is derived from the ancient Greek word for salt.

The saliferous underground strata quickly closed up after the abandonment of an mine adit (passageway), excellently preserving materials that usually are not durable (Beckel 1983). Due to modern salt mining, documented since 1311 AD, many prehistoric shafts were destroyed. However, numerous others were rediscovered, thus uncovering many objects made of leather and wood, as well as fabric remnants. $^{14}$C AMS measurements were performed on spruce logs from 3 different rediscovered mines to determine when salt mining began in Hallstatt.

**SAMPLE PREPARATION**

We describe below the sample preparation procedures at the 3 AMS laboratories involved in the Iceman measurements.

**Vienna, Austria**

First, the samples were cleaned mechanically by removing adherent particles with a scalpel and cleansing with bidistilled water in an ultrasonic bath. Next, the AAA (acid-alkali-acid) method was applied to the Iceman and Hallstatt samples (see e.g. Bonani et al. 1994; Wild et al. 1998). All the samples except 2 were successively treated with 1 M HCl, 0.1 M NaOH and 1 M HCl. Each pretreatment step was performed for 1 h at 60 °C; between each step, and at the end, the samples were washed to neutral pH with bidistilled water. Our standard AAA method described above was slightly modified for 2 Iceman samples to avoid dissolution of the sample material. VERA-0056, a hair sample from an ibex (wild goat; see Table 1), was kept at room temperature during the alkaline step, and for VERA-0054 (leather, see Table 1), 0.01 M NaOH instead of 0.1 M NaOH was used and the entire AAA method was performed at room temperature. The blanks (specular graphite containing no $^{14}$C) and the IAEA standard materials C-3 cellulose and C-5 wood were also subjected to our standard procedure. The IAEA standard material C-6 sucrose was not pretreated.

After chemical pretreatment, the samples, standards and blanks (usually about 10 mg), together with some Ag wire, were put into a quartz vial containing 1 g Cu(II)O rodlets. The evacuated and flame-torch sealed vials were heated in an oven at 900 °C for 4 h. Following the method of Vogel et al. (1984) the resulting CO$_2$ was transferred to a graphitization system where the CO$_2$ was catalytically reduced with high-purity H$_2$ to elemental carbon on an iron powder catalyst ($< 200$ mesh) according to:

$$\text{(Fe, 580 °C)}$$

$$\text{CO}_2 + 2\text{H}_2 \rightarrow \text{C} + 2\text{H}_2\text{O}$$ (1)

The carbon-catalyst mixture of each sample was split up into 3 or 4 portions containing about 1 mg of carbon. They were pressed into Al target holders (drill holes 1.1 mm in diameter) with a recess of 0.5 mm. Two or 3 of them (i.e., duplicates or triplicates of the same sample) were used for the AMS measurements; the remaining targets were stored in an archive.

**Uppsala, Sweden**

Samples were cleaned mechanically first, removing visible particles, etc. Next, an AA (acid-alkali) method was applied: 1) 1% HCl for 6–8 h kept below the boiling point, 2) washing in distilled water,
3) 1% NaOH for 6–8 h kept below the boiling point, and 4) washing in distilled water. The remaining insoluble fraction was combusted with Cu(II)O at 800 °C for 10 min and graphitized using Fe and H₂ at 750 °C. Each of the 2 grass samples (Ua-2373 and Ua-2374) was pretreated uniformly, but 2 independent combustions and graphitizations for each sample were done (G Possnert, personal communication 1992).

**Gif-sur-Yvette, France**

All samples were divided into 2 or 3 subsamples, to which 2 different pretreatment procedures were applied: 1) an AAA method similar to the one applied in Vienna, and 2) a cellulose extraction method for the wood samples replacing the last acid step in step 1) by bleaching in NaClO₂ at 80 °C. Each subsample was also combusted and graphitized separately using Fe as a catalyst. The carbon-catalyst mixture yielded 2 or 3 targets with 1 mm diameter (M Arnold, personal communication 1998).

**14C AMS measurements**

In this paper, only the measurements performed at the VERA 3 MV Pelletron® accelerator (Kutschera et al. 1997; Priller et al. 1997) in Vienna are described in detail. Datings of the 2 grass samples Ua-2373 and Ua-2374 (previously published in Prinoth-Fornwagner and Niklaus 1994, but given here in much more detail in Table 1) were performed at the 7 MV EN tandem accelerator in Uppsala, Sweden (Possnert 1984). Another grass sample, 1 tree leaf sample and 6 wooden samples from the vicinity of the Iceman (see the GifA laboratory numbers in Table 1) were measured at the 3 MV Tandetron® accelerator in Gif-sur-Yvette (Arnold et al. 1987).

The datings at VERA comprised all the other Iceman samples specified in Table 1 as well as the wooden samples from Hallstatt shown in Table 2a. Samples were loaded into the 40-position target wheel of the Multi-Cathode SNICS sputter source (each position contains one target). ¹³C/¹²C and ¹⁴C/¹²C ratios were obtained by using the 3+ charge state at 2.7 MV terminal voltage. For details of the machine performance see Priller et al. (1997) and Rom et al. (1998).

The sample loading contained 9 samples from the Iceman (6 triplicates and 3 duplicates), 3 different IAEA standard materials (C-6 sucrose triplicates, C-5 wood duplicates, and C-3 cellulose triplicates) warranting a high level of quality control, 3 machine blank targets, i.e. “dead” graphite containing no ¹⁴C, and a chemistry blank duplicate, i.e. a machine blank pretreated and processed in the same way as the samples. The Hallstatt sample loading contained 10 samples (8 triplicates and 2 duplicates), C-6 sucrose and C-3 cellulose triplicates, 2 machine blanks and a chemistry blank quadruplicate. Each target was measured for 200 sec, 8 times. Two of the samples (VERA-0040 and VERA-0041) were measured in 2 consecutive target wheels. The upper limit for the error on counting statistics was about 0.5% for every target except blanks.

As a quality control of the chemistry processing and the machine setup in all the regular ¹⁴C dating measurements performed so far at VERA, a C-6 Sucrose standard has been compared to a C-3 Cellulose standard measured in the same target wheel (see Figure 4). The corresponding chemistry blanks provide the absolute ¹⁴C dating limit T_max for each laboratory. This limit is connected to the scatter of the blank ΔpMC_blank given in percent modern carbon (pMC, see Stuiver and Polach [1977]) via

\[
T_{\text{max}} = -8033 \ln \left( \frac{2 \Delta pMC_{\text{blank}}}{100} \right)
\]

(Compare with Mook and Streurmann [1983] or Donahue [1990a].)
Table 1  Summary of \(^{14}\)C dating results for samples taken from the Iceman’s equipment

<table>
<thead>
<tr>
<th>Archaeological find nr</th>
<th>Lab nr</th>
<th>Detailed localization</th>
<th>Dry weight (g)</th>
<th>Chemical pretreatment</th>
<th>(^{14})C age (yr BP)</th>
<th>(\delta^{13})C (‰)</th>
<th>(\chi^2/\chi^2)-test (95%)</th>
<th>Calibrated age ranges (yr BC)</th>
<th>Fraction of age range</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-91/16b</td>
<td>GifA-91413</td>
<td>Leaves, parallel sample to no. B-91/16a</td>
<td>0.09</td>
<td>AAA</td>
<td>4550 ± 60</td>
<td>-22(^e)</td>
<td>—</td>
<td>3500–3430</td>
<td>3380–3050</td>
</tr>
<tr>
<td>B-91/32</td>
<td>GifA-93033</td>
<td>Stiffening of the quiver</td>
<td>0.04</td>
<td>AAA</td>
<td>4690 ± 70</td>
<td>-29(^e)</td>
<td>4.82 / 5.99</td>
<td>3520–3320</td>
<td>3220–3100</td>
</tr>
<tr>
<td>B-91/33</td>
<td>GifA-93035</td>
<td>Wood from the pannier</td>
<td>0.05</td>
<td>AAA</td>
<td>4430 ± 60</td>
<td>-30(^e)</td>
<td>9.05 / 5.99</td>
<td>3550–2900</td>
<td>3520–3550</td>
</tr>
<tr>
<td>B-91/34</td>
<td>GifA-93038</td>
<td>Wood from the pannier</td>
<td>0.06</td>
<td>AAA</td>
<td>4710 ± 70</td>
<td>-32(^e)</td>
<td>4.40 / 5.99</td>
<td>3620–3600</td>
<td>3520–3350</td>
</tr>
<tr>
<td>B-91/35</td>
<td>GifA-93040</td>
<td>Wood from the bow</td>
<td>0.13</td>
<td>AAA</td>
<td>4540 ± 70</td>
<td>-27(^e)</td>
<td>3.53 / 5.99</td>
<td>3520–3410</td>
<td>3390–3310</td>
</tr>
<tr>
<td>B-91/36</td>
<td>GifA-93043</td>
<td>Wood from the axe-shaft</td>
<td>0.04</td>
<td>AAA</td>
<td>4440 ± 60</td>
<td>-31(^e)</td>
<td>0.46 / 5.99</td>
<td>3350–3010</td>
<td>2980–2920</td>
</tr>
<tr>
<td>B-91/37</td>
<td>GifA-93045</td>
<td>Wood from the pannier</td>
<td>0.21</td>
<td>AAA</td>
<td>4430 ± 70</td>
<td>-32(^e)</td>
<td>2.68 / 5.99</td>
<td>3350–3020</td>
<td>3550–2900</td>
</tr>
<tr>
<td>B-91/38</td>
<td>GifA-93047</td>
<td>Leaves from the ember vessel</td>
<td>0.08</td>
<td>AAA</td>
<td>4540 ± 70</td>
<td>-28(^e)</td>
<td>—</td>
<td>3550–2900</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\)AA = acid-alkali, AAA = acid-alkali-acid, Cellulose = acid-alkali + NaClO\(_2\) pretreatment. \(^b\)\(\chi^2\)-values, corresponding 95% confidence limits for 3 subsamples of the sample, which were independently chemically pretreated and graphitized. \(^c\)Calibration by OxCal v2.18 with default system options and the INTCAL98 calibration curve; 95.4% confidence ranges (2\(\sigma\)). \(^d\)Relative probability of finding the true age in the respective time range. The absolute probability is obtained by multiplying by 0.954 (2\(\sigma\) range). \(^e\)Error estimated to 3%.
Table 1  Summary of $^{14}$C dating results for samples taken from the Iceman’s equipment (Continued)

<table>
<thead>
<tr>
<th>Archaeological find nr</th>
<th>Lab nr</th>
<th>Specification</th>
<th>Species</th>
<th>Detailed localization</th>
<th>Dry weight (g)</th>
<th>Chemical pretreatment$^a$</th>
<th>$^{14}$C age (yr BP)</th>
<th>$\delta^{13}$C (%)</th>
<th>$X^2 / \chi^2$-test ranges (95%)$^b$</th>
<th>Calibrated age ranges (yr BC)$^c$</th>
<th>Fraction of age range$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-91/3</td>
<td>Ua-2373</td>
<td>Leaves</td>
<td>Grasses (Poaceae)</td>
<td>Grasses from the filling of his left shoe</td>
<td>0.13</td>
<td>AA</td>
<td>4620 ± 75</td>
<td>-26.0</td>
<td>0.02 / 3.84$^b$</td>
<td>3650–3100</td>
<td>1.00</td>
</tr>
<tr>
<td>B-91/16a</td>
<td>Ua-2374</td>
<td>Leaves</td>
<td>Grasses (Poaceae)</td>
<td>Grasses from the cape</td>
<td>0.07</td>
<td>AA</td>
<td>4250 ± 70</td>
<td>-24.5</td>
<td>3.80 / 3.84$^b$</td>
<td>3350–2650</td>
<td>1.00</td>
</tr>
<tr>
<td>B-91/35</td>
<td>VERA-0050</td>
<td>Wood from the bow, parallel sample to no. B-91/35</td>
<td>Yew (Taxus baccata)</td>
<td>Recovered during sample washing</td>
<td>—</td>
<td>AAA</td>
<td>4500 ± 30</td>
<td>-24.9 ± 1.2</td>
<td>0.01 / 3.84$^b$</td>
<td>3350–3090</td>
<td>1.00</td>
</tr>
<tr>
<td>91/96</td>
<td>VERA-0051</td>
<td>Wood</td>
<td>Hazel (C. avellana)</td>
<td>Recovered during sample washing</td>
<td>0.06</td>
<td>AAA</td>
<td>4520 ± 30</td>
<td>-27.2 ± 1.2</td>
<td>0.17 / 5.99$^b$</td>
<td>3360–3100</td>
<td>1.00</td>
</tr>
<tr>
<td>91/139</td>
<td>VERA-0053</td>
<td>Charcoal from the ember vessel</td>
<td>Conifers</td>
<td>Recovered during sample washing</td>
<td>0.27</td>
<td>AAA</td>
<td>4690 ± 40</td>
<td>-23.0 ± 1.9</td>
<td>0.08 / 3.84$^b$</td>
<td>3630–3580 / 3540–3360</td>
<td>0.15 / 0.85</td>
</tr>
<tr>
<td>91/139</td>
<td>VERA-0049</td>
<td>Leaves from the ember vessel, parallel sample to no. B-91/38</td>
<td>Norway Maple Tree (Acer platanoides)</td>
<td>Recovered during sample washing</td>
<td>0.06</td>
<td>AAA</td>
<td>4510 ± 40</td>
<td>-27.2 ± 1.8</td>
<td>0.11 / 3.84$^b$</td>
<td>3360–3090 / 3060–3040</td>
<td>0.98 / 0.02</td>
</tr>
<tr>
<td>92/181</td>
<td>VERA-0054</td>
<td>Leather</td>
<td>—</td>
<td>Recovered during sample washing</td>
<td>0.07</td>
<td>AAA</td>
<td>4480 ± 40</td>
<td>-22.1 ± 1.4</td>
<td>0.57 / 5.99$^b$</td>
<td>3350–3020</td>
<td>1.00</td>
</tr>
<tr>
<td>92/275</td>
<td>VERA-0048</td>
<td>Wood, binding material</td>
<td>Green Alder (Alnus viridis)</td>
<td>Found in the western part of the southern rock-rub</td>
<td>0.04</td>
<td>AAA</td>
<td>2500 ± 40</td>
<td>-24.9 ± 1.8</td>
<td>0.75 / 5.99$^b$</td>
<td>800–410</td>
<td>1.00</td>
</tr>
<tr>
<td>92/283</td>
<td>VERA-0056</td>
<td>Hair</td>
<td>Ibex (Capra ibex)</td>
<td>Sediment from the gully</td>
<td>0.49</td>
<td>AAA</td>
<td>4510 ± 30</td>
<td>-22.2 ± 1.7</td>
<td>0.13 / 5.99$^b$</td>
<td>3360–3090</td>
<td>1.00</td>
</tr>
<tr>
<td>92/283</td>
<td>VERA-0055</td>
<td>Mosses</td>
<td>Polytrichum sexangulare</td>
<td>Sediment from the gully</td>
<td>0.08</td>
<td>AAA</td>
<td>4700 ± 40</td>
<td>-23.0 ± 1.6</td>
<td>0.29 / 3.84$^b$</td>
<td>3640–3560 / 3540–3370</td>
<td>0.22 / 0.78</td>
</tr>
<tr>
<td>92/292</td>
<td>VERA-0052</td>
<td>Wood</td>
<td>Pine (Pinus sp.)</td>
<td>Found on the southern rock-rub</td>
<td>0.02</td>
<td>AAA</td>
<td>5820 ± 40</td>
<td>-21.0 ± 1.5</td>
<td>5.52 / 5.99$^b$</td>
<td>4780–4540</td>
<td>1.00</td>
</tr>
</tbody>
</table>

$^a$AA = acid-alkali, AAA = acid-alkali-acid, Cellulose = acid-alkali + NaClO$_2$ pretreatment. $^b$χ$^2$-values and corresponding 95% confidence limits for $^b$two independent graphitizations of the same chemically uniformly pretreated sample; $^b$several targets of a uniformly pretreated and graphitized sample. $^c$Calibration by OxCal v2.18 with default system options and the INTCAL calibration curve. The 95.4% confidence ranges (2σ) are given. Given $^{14}$C ages were rounded according to (Stuiver and Polach 1977) before calculating. $^d$Relative probability of finding the true age in the respective time range. The absolute probability is obtained by multiplying with 0.954 (2-σ range). $^e$δ$^{13}$C estimated, not measured.
Table 2a. Summary of $^{14}$C results for samples taken from logs in the salt mines of Hallstatt

<table>
<thead>
<tr>
<th>Lab nr</th>
<th>Archaeological identification nr (inventory nr)</th>
<th>Location (mining group)</th>
<th>Species</th>
<th>Weight (g)</th>
<th>$^{14}$C age (yr BP)</th>
<th>$\Delta^{13}$C (%)</th>
<th>$X^2 / \chi^2$-test (95%)</th>
<th>Calibrated age ranges (yr BC)</th>
<th>Fraction of age range</th>
</tr>
</thead>
<tbody>
<tr>
<td>VERA-0040</td>
<td>Hallstatt 1997/07 (77391)</td>
<td>Log #1, outermost rings (58–66)</td>
<td>Gruner mine</td>
<td>Northern</td>
<td>Spruce</td>
<td>0.071</td>
<td>3275 ± 35</td>
<td>−19.0 ± 0.7</td>
<td>0.63 / 3.84</td>
</tr>
<tr>
<td>VERA-0041</td>
<td>Hallstatt 1997/08 (77391)</td>
<td>Log #1, innermost rings (1–10)</td>
<td>Gruner mine</td>
<td>Northern</td>
<td>Spruce</td>
<td>0.183</td>
<td>3080 ± 35</td>
<td>−24.8 ± 0.8</td>
<td>2.58 / 3.84</td>
</tr>
<tr>
<td>VERA-0042</td>
<td>Hallstatt 1997/09 (73232D)</td>
<td>Log #2, outermost rings (40–49)</td>
<td>Gruner mine</td>
<td>Northern</td>
<td>Spruce</td>
<td>0.102</td>
<td>3040 ± 40</td>
<td>−20.9 ± 0.9</td>
<td>0.41 / 3.84</td>
</tr>
<tr>
<td>VERA-0039</td>
<td>Hallstatt 1997/06 (88887)</td>
<td>Log #3, outermost rings (68–76)</td>
<td>Gruner mine</td>
<td>Northern</td>
<td>Spruce</td>
<td>0.112</td>
<td>3020 ± 45</td>
<td>−20.8 ± 1.5</td>
<td>0.27 / 3.84</td>
</tr>
<tr>
<td>VERA-0043</td>
<td>Hallstatt 1997/10 (68795C)</td>
<td>Log #4, outermost rings (71–80)</td>
<td>Log house</td>
<td>—</td>
<td>Spruce</td>
<td>0.035</td>
<td>3070 ± 40</td>
<td>−22.3 ± 0.7</td>
<td>1.87 / 5.99</td>
</tr>
<tr>
<td>VERA-0035</td>
<td>Hallstatt 1997/02 (4842G)</td>
<td>Log #5, innermost rings (1–10)</td>
<td>Appold mine</td>
<td>Northern</td>
<td>Spruce</td>
<td>0.371</td>
<td>3035 ± 40</td>
<td>−23.9 ± 1.2</td>
<td>0.47 / 5.99</td>
</tr>
<tr>
<td>VERA-0034</td>
<td>Hallstatt 1997/01 (4842G)</td>
<td>Log #5, outermost rings (41–50)</td>
<td>Appold mine</td>
<td>Northern</td>
<td>Spruce</td>
<td>0.140</td>
<td>3040 ± 45</td>
<td>−22.2 ± 1.3</td>
<td>2.93 / 5.99</td>
</tr>
<tr>
<td>VERA-0034 (after &quot;wiggle matching&quot; log #5 with VERA-0035 and VERA-0034)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>VERA-0038</td>
<td>Hallstatt 1997/05 (FNr.90)</td>
<td>Log #6, innermost rings (1–8)</td>
<td>Tuschi mine</td>
<td>Eastern</td>
<td>Spruce</td>
<td>0.256</td>
<td>2945 ± 35</td>
<td>−24.4 ± 1.1</td>
<td>0.89 / 5.99</td>
</tr>
<tr>
<td>VERA-0037</td>
<td>Hallstatt 1997/04 (FNr.90)</td>
<td>Log #6, intermediate rings (18–45)</td>
<td>Tuschi mine</td>
<td>Eastern</td>
<td>Spruce</td>
<td>0.156</td>
<td>2940 ± 40</td>
<td>−23.4 ± 1.4</td>
<td>0.71 / 5.99</td>
</tr>
<tr>
<td>VERA-0036</td>
<td>Hallstatt 1997/03 (FNr.90)</td>
<td>Log #6, outermost rings (70–80)</td>
<td>Tuschi mine</td>
<td>Eastern</td>
<td>Spruce</td>
<td>0.692</td>
<td>2920 ± 50</td>
<td>−24.3 ± 2.3</td>
<td>0.03 / 5.99</td>
</tr>
<tr>
<td>VERA-0036 (after &quot;wiggle matching&quot; log #6 with VERA-0038 and VERA-0036)</td>
<td></td>
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</tr>
</tbody>
</table>

*aAll samples received AAA pretreatment (acid-alkali-acid).

*b$X^2$-values and corresponding 95% confidence limits for 1) two independent measurements of targets of the same chemically uniformly pretreated sample mounted into different target wheels; 2) several targets of a uniformly pretreated and graphitised sample.

cCalibration by OxCal v2.18 with default system options and the INTCAL98 calibration curve. The 95.4% confidence ranges (2$\sigma$) are given.

dRelative probability of finding the true age in the respective time range. The absolute probability is obtained by multiplying with 0.954 (2-$\sigma$ range).
DATA EVALUATION AND CALIBRATION

Although AMS measurements were performed at 3 different AMS laboratories, only the data evaluation at VERA shall be discussed in detail (see also Kutschera et al. (1997); Priller et al. (1997); Rom et al. (1998)).

First, for each target \( j \), the mean values of the \(^{13}\text{C}/^{12}\text{C} \) (\( R_{13j} \)) and \(^{14}\text{C}/^{12}\text{C} \) (\( R_{14j} \)) ratios, respectively, and the corresponding standard deviations of the mean (\( S_{13j}, S_{14j} \)) were computed:

\[
R_{13j} = \frac{1}{m_j} \sum_{k=1}^{m_j} R_{13j,k}; \quad R_{14j} = \frac{1}{m_j} \sum_{k=1}^{m_j} R_{14j,k}
\]

\[
S_{13j} = \sqrt{\frac{1}{m_j(m_j-1)} \sum_{k=1}^{m_j} (R_{13j,k} - R_{13j})^2} ; \quad S_{14j} = \sqrt{\frac{1}{m_j(m_j-1)} \sum_{k=1}^{m_j} (R_{14j,k} - R_{14j})^2}
\]

where \( R_{13j,k} \) denotes the \(^{13}\text{C}/^{12}\text{C} \) ratio of the \( k \)th measurement on the \( j \)th target, \( R_{14j,k} \) the corresponding \(^{14}\text{C}/^{12}\text{C} \) ratio, \( m_j \) is the number of measurements performed at target \( j \), \( S_{13j} \) stands for the standard deviation of \( R_{13j} \), \( S_{14j} \) for the standard deviation of \( R_{14j} \).

The error for each target originating in counting statistics only can be written as

\[
S_{statj} = \sqrt{\frac{1}{m_j} \sum_{k=1}^{m_j} (S_{statj,k})^2}
\]

where \( S_{statj,k} \) denotes the counting statistical error of the \(^{14}\text{C}/^{12}\text{C} \) ratio of the \( k \)th measurement on the \( j \)th target, \( ^{12}\text{C}^{3+}_{j,k} \) is the corresponding number of \(^{12}\text{C}^{3+} \) ions.

In the next step, for all targets containing the same sample material, the weighted mean \( R \) of the \(^{13}\text{C}/^{12}\text{C} \) (\( R_{13} \)) and the \(^{14}\text{C}/^{12}\text{C} \) (\( R_{14} \)) ratios, respectively, and the corresponding internal and the external errors (\( S_{int} \) and \( S_{ext} \)) are computed. When calculating these weighted means, for the \(^{13}\text{C}/^{12}\text{C} \) ratios \( S_j \) in (5) is replaced by \( S_{13j} \), in the case of \(^{14}\text{C}/^{12}\text{C} \) ratios \( S_j \) is replaced by the larger of the two errors \( S_{14j} \) and \( S_{statj} \).

\[
R = \frac{\sum_{j=1}^{n} R_j}{\sum_{j=1}^{n} (S_j)^2}, \quad S_{int} = \sqrt{\frac{\sum_{j=1}^{n} \frac{1}{(S_j)^2} (R_j - R)^2}{(n-1) \sum_{j=1}^{n} (S_j)^2}}, \quad S_{ext} = \sqrt{\frac{\sum_{j=1}^{n} \frac{1}{(S_j)^2} (R_j - R)^2}{(n-1) S_{int}^2}}
\]
For the $\delta^{13}C$ corrections we use the following definitions

$$
\delta^{13}C_{\text{sample}} = \left( \frac{R^{13}_{\text{sample}} - R^{13}_{\text{PDB}}}{R^{13}_{\text{PDB}}} \right) 1000\% \text{; } \delta^{13}C_{\text{std}} = \left( \frac{R^{13}_{\text{std}} - R^{13}_{\text{PDB}}}{R^{13}_{\text{PDB}}} \right) 1000\% \quad (7a, 7b)
$$

where the subscript $\text{PDB}$ denotes the PDB standard and $\text{std}$ the standard material (usually C-3 cellulose) to which our measurements are referenced. The $\delta^{13}C_{\text{std}}$ is the recommended IAEA value of this particular standard material.

Eliminating $R^{13}_{\text{PDB}}$ results in

$$
\delta^{13}C_{\text{sample}} = \left( \frac{R^{13}_{\text{sample}}}{R^{13}_{\text{std}}} \left( 1 + \frac{\delta^{13}C_{\text{std}}}{1000} \right) - 1 \right) 1000\%. \quad (8)
$$

The corresponding error is obtained by using Gauss's equation for propagation of errors considering correlations.

Finally, the $^{14}C^{3+}/^{12}C^{3+}$ ratios of the samples, standards and blanks are normalized to $\delta^{13}C = -25\%$ (Stuiver and Polach 1977) by the quadratic form of the fractionation correction (see Stuiver and Robinson 1974)

$$
R^{14}_{25,x} = R^{14}_x \left[ \frac{1 - 25}{1000} \frac{\delta^{13}C_x}{1000} \right] ^2 , \quad (9)
$$

where the subscript $x$ holds for sample, std or blank.

The following background correction was used:

$$
pMC_{\text{sample}} = pMC_{\text{recommended}} \frac{(R^{14}_{\text{sample},-25} - R^{14}_{\text{blank},-25})}{(R^{14}_{\text{std},-25} - R^{14}_{\text{blank},-25})} . \quad (10)
$$

$pMC_{\text{recommended}}$ is the pMC value recommended by the IAEA for the particular standard material. The corresponding error again is obtained by using Gauss's equation for propagation of errors considering correlations.

This correction is valid for the following assumptions: a) the carbon masses of the sample, the standard and the blank material are all the same, and the contamination is equal for all those materials (in mass and in isotopic composition), or the carbon masses for all these materials may be different, but the contamination is strictly proportional to the mass; b) the portion of extraneous modern carbon, i.e. carbon with an $^{14}C^{12}C$ ratio of about $1.2 \times 10^{-12}$ or $100$ pMC, introduced as contamination is small compared to the sample, to the standard and to the blank size. This contaminating carbon is known to be in the range of a few µg (Vogel et al. 1987; Donahue et al. 1990b), compared to a few mg target size. From the data shown in Figure 4c it can be deduced that for samples at the 5-mg level, typically processed at VERA, the corresponding contamination amounts to about 15 µg modern carbon.
It is interesting to note that equation (6b) can be rearranged as

$$\sum_{j=1}^{n} \frac{I}{(S_j)^2} (R_j - R)^2 = \frac{(S_{ext})^2}{(S_{int})^2} (n - 1).$$  (11)

Assuming that the \( R_j \) are independent, normally distributed random variables with mean value \( R \) and standard deviations \( S_j \), the sum on the left side is \( \chi^2 \)-distributed with \( (n-1) \) degrees of freedom (see e.g. Martin 1971; Ward and Wilson 1978). Therefore, one can use this sum in a \( \chi^2 \)-test for checking the hypothesis \( H_0 \) that the data \( R_j \) stem from the same normally distributed parent population with mean value \( R \) vs. the alternative hypothesis \( H_1 \). The \( R_j \) all can have different standard deviations \( S_j \), reflecting different levels of precision in measuring the data. If the limit for a given confidence level (usually 95%) is exceeded by the sum in (11), \( H_1 \) is preferred to \( H_0 \). One should keep in mind that \( ^{14}C \) ages are in principle not normally distributed (like the pMC values), but if the ages to be averaged do not differ too much the \( \chi^2 \)-test can be applied directly to the BP values (see Ward and Wilson 1978).

Tables 1 and 2a show the results for all measurements of the Iceman and the Hallstatt samples. Table 2b gives a comprehensive summary of already published dates from the beginning of salt mining in Hallstatt. Conversion of all the \( ^{14}C \) ages to calendar ages given in this paper and also the “wiggle matching” of the spruce log samples from Hallstatt have been performed via the calibration program OxCal v2.18 (Ramsey 1995a, 1995b) using the default system options (cubic smoothing of the calibration curve, rounding off of the calibrated age ranges, etc.) and the INTCAL98 \( ^{14}C \) calibration curve (Stuiver et al. 1998). \( ^{14}C \) ages were rounded off according to Stuiver and Polach (1977) before calibrating. The so-called “wiggle matching” (referring to “wiggles” in the calibration curve, which originate in the varying \( ^{14}C \) content of the atmosphere) is a useful procedure in combining dates from several pieces of wood stemming from the same log. Since the difference in calendar age between this pieces is known via the tree-ring sequence, this additional information can be used to obtain more accurate dates (Ramsey 1995b).

Table 2b. Summary of already published \( ^{14}C \) results for samples taken from the oldest parts of the salt mines of Hallstatt

<table>
<thead>
<tr>
<th>Lab nr</th>
<th>Site</th>
<th>Location (mining group)</th>
<th>Specific description</th>
<th>( ^{14}C ) age (yr BP)</th>
<th>Reference</th>
<th>Calibrated age ranges (yr BC)(^a)</th>
<th>Fraction of age range(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GrN-19975</td>
<td>Grüner mine</td>
<td>Northern</td>
<td>—</td>
<td>3077 ± 13</td>
<td>Barth (1993–94)</td>
<td>1410–1260</td>
<td>1.00</td>
</tr>
<tr>
<td>GrN-6047</td>
<td>Grüner mine</td>
<td>Northern</td>
<td>—</td>
<td>2950 ± 35</td>
<td>Barth (1974)</td>
<td>1300–1020</td>
<td>1.00</td>
</tr>
<tr>
<td>VRI-345</td>
<td>Grüner mine</td>
<td>Northern</td>
<td>Pick handle</td>
<td>2810 ± 90</td>
<td>Barth (1974)</td>
<td>1260–1240</td>
<td>0.01</td>
</tr>
<tr>
<td>GrN-19842</td>
<td>Grüner mine</td>
<td>Northern</td>
<td>—</td>
<td>2880 ± 35</td>
<td>Barth (1993–94)</td>
<td>1210–920</td>
<td>1.00</td>
</tr>
<tr>
<td>VRI-267</td>
<td>Flechner mine</td>
<td>Northern</td>
<td>Fire-sticks</td>
<td>2920 ± 100</td>
<td>Felber (1973)</td>
<td>1400–800</td>
<td>1.00</td>
</tr>
<tr>
<td>GrN-19840</td>
<td>Tusch mine</td>
<td>Eastern</td>
<td>—</td>
<td>2980 ± 50</td>
<td>Barth (1993–94)</td>
<td>1380–1020</td>
<td>1.00</td>
</tr>
<tr>
<td>GrN-19973</td>
<td>Tusch mine</td>
<td>Eastern</td>
<td>—</td>
<td>2966 ± 16</td>
<td>Barth (1993–94)</td>
<td>1260–1120</td>
<td>1.00</td>
</tr>
<tr>
<td>VRI-558(^c)</td>
<td>Kaiser-Josef-adit (Kilb mine(^d))</td>
<td>Eastern</td>
<td>Twigs</td>
<td>2990 ± 100</td>
<td>Felber (1973)</td>
<td>1450–900</td>
<td>1.00</td>
</tr>
<tr>
<td>VRI-258</td>
<td>Kaiser-Josef-Querschlag I</td>
<td>Eastern</td>
<td>Wooden fragment of a tool</td>
<td>2810 ± 90</td>
<td>Felber (1973)</td>
<td>1260–1240</td>
<td>0.01</td>
</tr>
</tbody>
</table>

\(^a\)Calibration by OxCal v2.18 with default system options. The 95.4% confidence ranges (2 \( \sigma \)) are given. Given \( ^{14}C \) ages were rounded according to (Stuiver and Polach 1977) before calibrating.

\(^b\)Relative probability of finding the true age in the respective time range. The absolute probability is obtained by multiplying with 0.954 (2-\( \sigma \) range).

\(^c\)Marked as unexpectedly high in (Felber 1973) and discarded as a statistical outlier in (Barth 1993–94).

\(^d\)See Barth (1993–94).
All except 1 of the averaged $^{14}$C ages shown in Table 1 are weighted averages. The corresponding errors for the Gif-sur-Yvette samples are internal errors, only if the 95% confidence limit of the above-mentioned $\chi^2$-test is exceeded the unweighted mean and the corresponding standard deviation is given (see archaeological find number B-91/33 in Table 1). The averaged $^{14}$C ages of the samples measured at Vienna and also of those measured at Uppsala were determined as described above using the larger of the internal and external errors.

![Figure 1](https://example.com/figure1.png)

**Figure 1** The “Iceman” samples. Horizontal bars indicate 95.4% confidence ranges (2σ), the dashed vertical lines show the 2-σ range obtained from tissue and from bone samples measured at the AMS laboratories of Zurich, Switzerland and of Oxford, England (see text).

**THE ICEMAN**

Table 1 and Figure 1 show the results of the Iceman samples that originate from 2 excavations in the vicinity of “Otzi” in 1991 and 1992 (Lippert 1992; Bagolini et al. 1995). The grass samples were taken at the Institute for Forensic Medicine at the University of Innsbruck 1 week after the salvage of the Iceman; all the other samples were taken at the Römisch-Germanisches Zentralmuseum in Mainz in 1991 and 1997. The samples consist mainly of wooden material, but also mosses and leather were dated. The bulk of these samples confirms the time period of 3360–3100 BC previously determined from bone and tissue specimens from the Iceman (Bonani et al. 1992, 1994; Hedges et al. 1992; Prinoth-Fornwagner and Niklaus 1994). However, for 2 wooden samples, clearly deviating dates were found: 790–410 BC (VERA-0048) and 4790–4550 BC (VERA-0052). These samples provide evidence that the site of the Iceman was used as a mountain pass 1500 yr earlier, i.e. at the transition of the Mesolithic to the Neolithic period, confirming an archaeological presumption expressed earlier (Bagolini et al. 1995), and 2000 yr later, i.e. in the Hallstatt period (Figure 1, Table 1). Especially interesting is the younger sample, showing clear working traces (K Oeggl, personal communication 1998). It is the first artifact from the Iron age found in this Alpine region (Kutschera et al. 1998).
The first dates on botanical remains were published in Egg and Spindler (1992). However, information on these findings (e.g. botanical specification) is incomplete. Also, no reference to the calibration curve used and the calibration procedure is given. $^{14}$C ages are not given either. This makes it difficult to include these dates in a general comparison. Nevertheless, for completeness, we list these results here: Uppsala/S 3053–2931 BC (1σ) corresponds to Ua-2374 (G Possnert, personal communication 1992) (see Table 1), Paris/F 3365–3106 BC (1σ) is likely to be GifA-91413 (Table 1), Cambridge/Mass. USA 3362–3136 BC (1σ), 3492–3049 BC (2σ) presumably is GX-18504-AMS (see Prinloh-Fornwagner and Niklaus 1994 and below).

Sample GifA-91402 published in Prinloh-Fornwagner and Niklaus (1994) should be discarded, since according to M Arnold (personal communication 1995) the sample burnt was very small and the contamination was certainly larger than normal. A re-calibration of 2 further grass samples, ETH-8345.3 (4535 ± 60 BP, $\delta^{13}$C = (−25.4 ± 0.9)‰, 1.5 mg sample size, AAA pretreatment)

\[1\] A combined calibration of the weighted means for tissue (4523 ± 27 BP) and bone samples (4576 ± 27 BP) determined at the AMS laboratories of Zurich and Oxford was performed using a time shift of 20 yr for the mean carbon turnover time in bone collagen (see Bonani et al. 1992; Hedges et al. 1992). Calibration yields time ranges of 3350–3320 BC (0.72), 3190–3170 BC (0.12), 3140–3120 BC (0.17) for the 68.2% confidence interval, and 3360–3310 BC (0.63), 3200–3100 BC (0.37) for the 95.4% confidence interval; the numbers in brackets denote the relative probability of finding the true age in the respective time range.
(Bonani et al. 1994) and GX-18504-AMS (4555 ± 48 BP, δ¹³C = −25.5‰) (Prinoth-Fornwagner and Niklaus 1994), yields 3500–3460 BC (0.03), 3380–3020 BC (0.97) and 3500–3460 BC (0.06), 3380–3090 BC (0.94) for the 95.4% confidence intervals; the numbers in brackets following calibrated age ranges denote the relative probability of finding the true age in the respective time range.

Figure 3 Comprehensive survey of ¹⁴C dates of wooden objects from the beginning of salt mining in Hallstatt. Both 1-σ and 2-σ ranges for single calibrated ¹⁴C dates are shown. VRI-558 and VERA-0040 have been omitted from this figure as outliers (see footnotes in Table 2b and text, respectively). VRI = Vienna Radium Institute, GrN = Centrum voor Isotopen Onderzoek, Groningen.

THE SALT MINES OF HALLSTATT

The ¹⁴C dating of objects presumably originating from the beginning of salt mining in Hallstatt, comprised spruce logs from 3 different prehistoric salt mines and a nearby log cabin on the surface. Two of these mines, the “Appold” and the “Grüner”, were rediscovered in 1879 and 1910, respectively (Barth 1993; Barth and Neubauer 1993). They are located in the Northern mining group, which is considered to be the oldest part of the salt mining field of Hallstatt.

The 3rd mine, the “Tusch”, was first discovered in 1748 and then rediscovered in 1991 (Barth 1993–1994). Two further samples shown in Figure 3 from the “Flechner” mine and the “Kaiser-Josef-Querschlag I” also belong to the oldest objects found in the salt mines of Hallstatt. The wane (Waldkante) of all logs shown in Figure 2 and Table 2a was still preserved. This enables a direct dating of the felling of the trees without any age offset. Usually, the timber was used only once (presumably) without any preceding storage (P Stadler, personal communication 1999). For all the other samples from Hallstatt (Table 3) no information concerning the trimming of the timbers or the presence of bark or sapwood has been published.

The ¹⁴C dates from the “Tusch” mine (Figures 2 and 3, Table 2a) including “wiggle matching” with OxCal v2.18 (Ramsey 1995b) set the beginning of the extraction of salt to the Late Bronze Age, i.e
the Early Urnfield period. This agrees with data from the same mine published earlier in Barth 1993–94 (see Table 2b, Figures 2 and 3). However, from the 14C dates of findings in the Northern mining group (including “wiggle matching”) one can infer that salt mining had already started in the Northern mining group in the 14th–13th century BC (see the “Grüner” and “Appold” mines in Figures 2 and 3, and Tables 2a and 2b). This corresponds to the transition of the Middle to the Late Bronze Age, i.e. the transition from the Tumulus to the Urnfield period (Lippert 1985). Sample GrN-19975 (see Figure 3) from the “Gruner” mine, which has been discarded as a statistical outlier in Barth 1993–1994, is now well confirmed by the dates obtained at VERA. Therefore, the beginning of salt mining in Hallstatt has to be set 1 to 2 centuries earlier than supposed so far (Barth 1993–94). The even higher age of 1 tree-ring set (see VERA-0040 in Figure 2) remains unexplained, but may reflect some non-removable contamination and therefore resists a reliable “ wiggle matching”.

![Figure 4](https://doi.org/10.1017/S0033822200019536)

**CONCLUSION**

Botanical remains from the vicinity of the Iceman, including his equipment, were dated at 3 different AMS laboratories. They show reasonable agreement with dates previously obtained on the tissue and bones of the Iceman himself. Two clearly deviating “outliers” indicate that the discovery site of Ötzi had been used as a mountain pass 1500 yr before the lifetime of the Iceman, and also 2000 yr later. The latter date is particularly interesting, because it constitutes the first artifact from the Iron Age in the entire Ötztal region. Spruce logs from the world’s oldest salt mines at Hallstatt, Austria were subject to 14C dating with AMS. The results from VERA provide evidence that salt mining at Hallstatt started 1–2 centuries earlier than previously supposed, i.e. in the 14th to the 13th century BC.
A current project at VERA carried out in cooperation with the Institute for Botany in Innsbruck, Austria deals with more than 50 additional samples from the site of the Iceman discovery. Besides leather and droppings from animals, the samples include mainly botanical remains such as mosses, grasses, and saxifrages. 14C dating of high Alpine plants may give information about glaciation and possible deglaciation periods at the rock depression where the Iceman died. From these dates, indirect evidence for the climate of the last 5000 yr may be obtained.

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REFERENCES


Felber H. 1973. Altersbestimmungen nach der Radio-
Dating Equipment from the Iceman


Ramsey CB. 1995b. OxCal Program v2.18. URL: <http://units.ox.ac.uk/departments/rlaha/oxcal/oxcal_h.html>.


