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RADIOCARBON DATING TO A SINGLE YEAR BY MEANS OF RAPID ATMOSPHERIC ^{14}C CHANGES

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ABSTRACT. In the best case, radiocarbon measurements allow artificial objects to be dated with a precision of 10 calendar years when conventional wiggle-matching onto the IntCal09 calibration curve is applied. More precise dating can only be achieved by using annually resolved ^{14}C calibration data, particularly in timespans when there are rapid changes in atmospheric ^{14}C concentration. The recently observed jump in atmospheric ^{14}C concentration of 1.5% between AD 774 and 775, though expected to be rare, is a good example for such a rapid change. We demonstrate by example that is possible to precisely ^{14}C date the cutting year of a timber in the historically important and well-preserved Holy Cross chapel of the convent St. John the Baptist in Val Müstair, Switzerland.

INTRODUCTION

The St. John convent in Müstair in the southeastern part of Switzerland was founded at the time of Charlemagne (AD 742–814) (Goll 2010). The convent with its well-preserved early Medieval frescos is listed as a UNESCO Word Heritage Site and was intensively archaeologically studied over the last several decades. The Holy Cross chapel of the St. John's convent (Figure 1a) represents an exceptional building in art history with its marble, plastering, and painting decorations (Goll 2013). It was first assigned to the Romanesque epoch, based on a comparison in style and the interpretation of historical data. The archaeological stratigraphy then showed that the chapel was built before AD 1000 and maybe even in the Carolingian era after the eastern wing of the Carolingian convent was built in the last quarter of the 8th century. The two-floor building with its trefoil-shaped plan is nearly completely extant. Even the wooden intermediate floor still exists (see Figure 1b), and this is most likely the oldest dated wooden-beamed ceiling in Europe.

The chapel was dated based on 18 dendrochronologically matching wooden beams. A total of 11 larch beams (*Larix decidua*) with waney edges were dated to be cut in the years AD 785–788 according to dendrochronological analyses of the Laboratoire Romand de Dendrochronologie (LRD) in Moudon, Switzerland (Hurni et al. 2007). A charred beam stump from a wall lath of the upper lost beamed ceiling (Figure 2) was sitting relatively loosely in the masonry, indicating that the beam was not yet fully dry when built in. This indicates the date of construction must have been 1–3 yr after the trees were cut and is thus relatively precisely known.

Only a few absolutely dated objects are available in art history for the Carolingian epoch (Oswald et al. 1990; e.g. Pace 2010). An accurate dating of the Holy Cross chapel is of extraordinary value Europe-wide, because it may answer questions of dating with respect to architecture, murals, marble sculptures, and stuccos, and even questions of local history. Therefore, scientific ethics require a validation of the dendrochronological data by means of a qualified second measurement. Three additional dendrochronology laboratories with experience in alpine timber were asked to verify independently the dating by LRD. However, all three laboratories failed to deliver a date based on dendrochronological techniques. In a second round, three radiocarbon laboratories were then asked

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Figure 1 (a) The Holy Cross chapel of the St. John convent; (b) the dated wooden beam ceiling

to determine a date. The conventional ^{14}C dating gave only inaccurate dates when calibrated with the ^{14}C calibration curve IntCal09 (Reimer et al. 2009) and thus could also not confirm the precise historical age.

Presently, IntCal09 is predominantly based on ^{14}C measurements of decadal dendrochronologically dated wood samples. The decadal sampling, as well as the mathematical routines used in the calibration curve, removes high-frequency changes (<10 yr) in atmospheric ^{14}C content and attenuates short-term changes in the measured raw data, respectively. This significantly limits the precision of ^{14}C wiggle-matching (Bronk Ramsey et al. 2001). However, the atmospheric ^{14}C concentrations

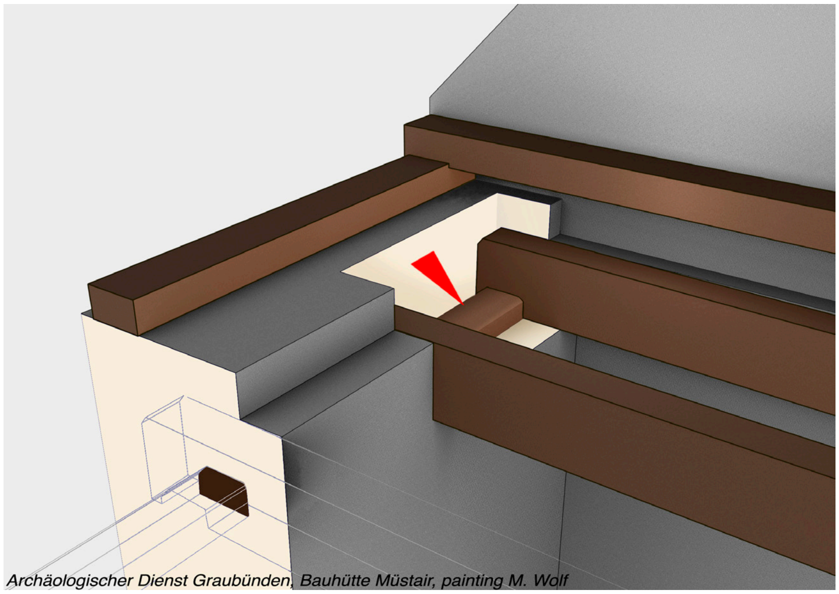

Figure 2 The drawing shows the location of the dated wall lathe (M06/24'255) in the wooden beam ceiling of the Holy Cross chapel.

in the past showed significantly more fine structure than is apparent in today's calibration curve. Excellent examples are the recent observations of a sudden 1.5% increase in atmospheric ^{14}C concentration between AD 774 and 775 (Miyake et al. 2012) and the 0.9% increase between AD 993 and 994 (Miyake et al. 2013). These events were strongly attenuated by the decadal sampling used for the IntCal calibration curve and thus, as such, were not recognized before. Any temporal fine structure will potentially allow temporal high-resolution wiggle-matching (HR wiggle-matching) to be performed. A confirmation of the dendrochronologically determined age of the Holy Cross chapel in Müstair is considered to be an ideal example demonstrating the power of HR wiggle-matching, because the years AD 774–775 should be present in the available wood and the chapel is historically a very important building.

METHOD

Sample Preparation for Radiocarbon Measurements

Wood samples of approximately 50 mg were cut by the LRD from annual tree rings of a wall lath of the Holy Cross chapel of the St. John convent in Müstair (Switzerland) for the ^{14}C analyses. The selected lath (see Figure 3) shows clearly the last grown ring of the tree (waney edge). The sampled larch (*Larix decidua*) shows strong drops in growth for the years AD 737, 753, and 777. Annual samples for the years 769 to 776 were cut with a razor blade (marked in red in Figure 3).

A base-acid-base-acid-bleaching method was applied for cleaning and cellulose extraction (Němec et al. 2010a). Kauri wood (ETH-44660) and brown coal (ETH-38779) from Reichewalde (Germany) significantly older than 60 kyr served as reference processing blanks and a dendrochronologically dated ring (AD 1515, ETH-40759) of a Swiss pine was used as a secondary standard (Güttler et al. 2013). The blanks and secondary standards have been prepared in parallel applying the same cleaning steps. All samples and the unprocessed OX-II standards were graphitized on the fully automated graphitization equipment (AGE) system (Němec et al. 2010b; Wacker et al. 2010c).

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High-Precision Radiocarbon Measurements

For [14]C analysis with the MICADAS system, samples were inserted in cassettes with 22 sample positions (Wacker et al. 2010b). In addition to the wood samples, each sample cassette contained three processing blanks, two processed secondary pine standards, as well as five OX-II standards for normalization. The total measurement time for high-precision analysis at ETH Zurich is about 1 hr per sample, subdivided into groups of 10 times 50 s. The OX-II standards typically yield about 500,000 counts (C^- ion currents of 50 µA) and the samples 300,000 counts (<2‰ counting statistics) during measurement time.

Data analysis and evaluation is performed using the computer program BATS (Wacker et al. 2010a), which also allows verification of measured data by means of statistical tests. The uncertainties in [14]C age are derived from counting statistics, standard normalization, and sample preparation. The [14]C counts were background corrected with the processing blank ($F^{14}C$: 0.0035 ± 0.004, $n = 6$) and normalized with OX-I ($n = 7$) and OX-II ($n = 5$) standards. An additional uncertainty of 1‰ was added, estimated from a long-term laboratory statistic of measurements on processed secondary wood standards.

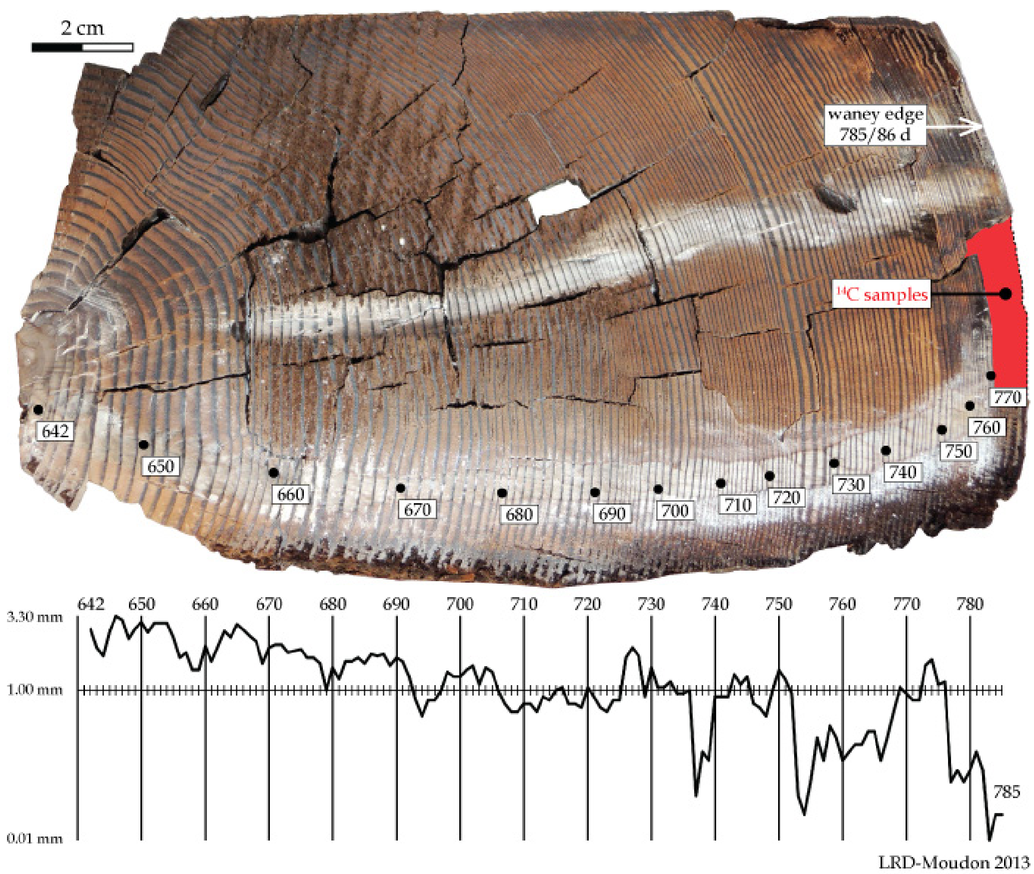

Figure 3 The sampling for [14]C dating (AD 769–776) and the dendrochronological signature of the wall lathe are shown. The first and last ring of this lathe dated to AD 642 and 785, respectively, based on the LRD dating.

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RESULTS AND CONCLUSIONS

The measured ^{14}C concentrations for the tree-ring samples of the Holy Cross chapel are given in Table 1. A sudden increase in ^{14}C concentrations (F^{14}C values) of more than 1% is evident between sample ETH-50136 (presumed age AD 774) and ETH-50137 (presumed age AD 775), both measured in duplicate. The data are compared in Figure 4 with the IntCal09 calibration curve (Reimer et al. 2009) and a self-made high-temporal resolution calibration curve (HR curve) with the mean of published dendrochronologically dated, annually resolved tree-ring measurements from Japan (Miyake et al. 2012) and Europe (Usoskin et al. 2013) around the AD 774–775 event.

Table 1 ^{14}C concentrations measured for the investigated tree-ring samples are given. The dendro age is the age obtained by dendrochronology that is to be confirmed.

Sample nr	F^{14}C	^{14}C age (BP)	δ^{13}C* (‰)	Dendro age
ETH-50131	0.8493 ± 0.0019	1312 ± 18	–20.1	AD 769
ETH-50133	0.8532 ± 0.0019	1275 ± 18	–22.1	AD 771
ETH-50134.1.1	0.8520 ± 0.0019	1287 ± 18	–21.4	AD 772
ETH-50134.1.2	0.8517 ± 0.0019	1289 ± 18	–21.5	AD 772
ETH-50135	0.8486 ± 0.0019	1319 ± 18	–22.3	AD 773
ETH-50136.1.1	0.8548 ± 0.0019	1260 ± 18	–22.4	AD 774
ETH-50136.1.2	0.8557 ± 0.0020	1252 ± 19	–23.4	AD 774
ETH-50137.1.1	0.8666 ± 0.0019	1150 ± 17	–21.2	AD 775
ETH-50137.1.2	0.8662 ± 0.0019	1154 ± 18	–21.8	AD 775
ETH-50138	0.8654 ± 0.0019	1161 ± 17	–20.9	AD 776

*The δ^{13}C value was measured on MICADAS with an accuracy of 1–2‰.

Chapel ^{14}C samples are matched to the HR curve such that the chi-square ($\chi(x)^2$) becomes minimal for an assumed age x for the outermost tree ring (waney edge):

$$\chi(x)^2 = \sum_{i=1}^{n} \frac{\left(R_i + \bar{C}(x - r_i)\right)^2}{\delta R_i^2 + \delta\bar{C}(x - r_i)^2}$$

where $R_i \pm \delta R_i$ are the measured values for the measured ^{14}C concentrations of the sample and $\bar{C}(x - r_i) \pm \delta\bar{C}(x - r_i)$ represents the ^{14}C concentrations of the HR curve for the year $(x - r_i)$, where r_i is the tree-ring number starting with ring number 0 as the last ring of the tree. The chi-squared for the most likely matches are given in Figure 5. A perfect match with a χ^2 of 9.1 ($n = 10$, $\chi^2_{red} = 0.91$) is obtained when the last ring of the sample tree is set to x = AD 785. A shift of 1 yr to younger ages ($x = 786$) is the second-best option and increases the χ^2 to 36.6. This, however, is statistically extremely unlikely (95% limit: $\chi^2 = 19.1$).

We can thus conclude that the wooden beam of the Holy Cross chapel in Val Müstair is absolutely dated with ^{14}C measurements to be cut after the ring for AD 785 was completed in autumn/winter AD 785/786. The results confirm precisely the dendrochronological dating performed by the LRD. All other timbers can doubtlessly be synchronized to the dated timbers because they have grown in the same region and show the same ecological characteristics. Subsequently, research in the archaeological building has found strong evidence supporting that timbers were built into houses within 1–3 yr after they were cut (Hollstein 1980). Also, it would appear implausible for the bent timbers required for the apsis of the chapel to have originated from recycled wood. Consequently, the chapel can now be historically recorded with certainty.

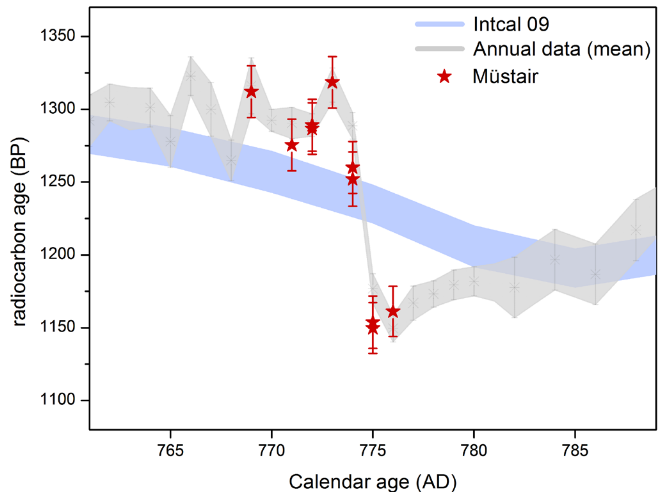

Figure 4 ^{14}C measurements of the tree-ring samples from Müstair are plotted onto the IntCal09 calibration curve and the mean of annually resolved tree-ring data of trees of Japan and Europe (Usoskin et al. 2013).

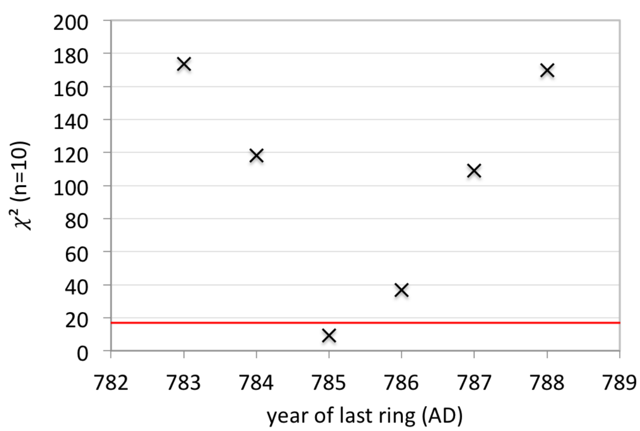

Figure 5 Chi-square test of the measured ^{14}C results are given for the most likely positions of the last ring, when matched to the mean of annually resolved tree-ring data of trees of Japan and Europe (Usoskin et al. 2013). The red line is the upper limit for the 2σ range for the 10 measured data points (10 degrees of freedom).

The presented example was performed on only seven samples, of which three were repeated for quality control (same pretreatment but repeated combustion, graphitization, and measurement). The five samples before the (expected) AD 774–775 event and the two samples after were clearly sufficient. One can even conclude that sampling the 2 yr before and the 2 yr after the 774–775 event would have been enough for an absolute date in this case, where the previously available date had to be confirmed. Here it should be noted that if the position of the 774–775 event within the sample series is not known, significantly more ^{14}C analyses are required. In such a case, we would propose to perform a traditional wiggle-match over a longer time period (sequence of 5–10 annual samples with gaps of ~6–10 yr). This would allow the region where the 774–775 event occurred to be determined. Annual measurement of the gap should then show the precise position of the AD 774–775 event. Such an exercise would require approximately 15 to 20 annual ^{14}C samples.

SUMMARY

The presented example of high temporarily resolved wiggle-matching ^{14}C dating of a wooden beam from the Holy Cross chapel with the use of the AD 774–775 event confirms absolutely the dendrochronological position and solves in an innovative and elegant way the delicate problem of reproducibility in dendrochronological dating. The waney edge of the wooden beam was dated precisely to the winter of AD 785/786. Statistically, there is no other possible match for the measured annual tree rings onto the data set of annually resolved calibration data previously measured in trees from Germany and Japan. However, we admit in the case where no supposed age information is previously available, more measurements are required to actually find the AD 774–775 event in a tree, if available at all. The benefit of such an exercise is, however, an extremely precise or even absolute date that may be of extraordinary value.

The Holy Cross chapel in Müstair is herewith one of the most precisely dated Carolingian buildings. The date sets an important measure for the well-preserved furnishings, such as wall paintings and stuccos, that originate from the time of construction.

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