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Chapter 10: Radiocarbon Dating of *Tsakali* Paper

Abstract: This chapter discusses the possibilities and limitations of the radiocarbon accelerator mass spectrometry (AMS) dating applied to date the Zhangzhung Nyengyü *tsakali* collection (the set of sixty-five initiation cards). Our report discusses the specificity of dating paper as a material, including the sample preparation (extraction of cellulose), the development of the AMS method that allows for minimising the size of the samples, and how to read the calibration line of ^{14}C dates.

1 The *tsakali* paper

The objects of the radiocarbon dating are two Tibetan initiation cards (*tsakali*) selected from the set of sixty-five belonging to the Zhangzhung Nyengyü system of the Bon religion, the subject of this book. On the recto sides, they bear the polychrome image of a divinity, saint or sacred object, and on the verso sides, a passage of text of varying length citing a scripture related to the corresponding image.

This Zhangzhung Nyengyü *tsakali* set is not conclusively dated by its text or other features that would allow for sure dating. The art-historical analysis by Christian Luczanits (see Chapter 3) suggests that the style of painting could have been commonly associated with the fourteenth century. However, this style is archaising, and some of the elements found in some figures – such as the lower garment of the Buddha's clothing – indicate a somewhat later date. Some figures depicted on the *tsakali* were possible to identify, so we know that these cards were not painted before the lifetimes of these people, but we could not say when these people were depicted. Further, X-ray scattering methods suggest the use of the blue pigment, that is a mixture of indigo and a previously undiscovered pigment, designated as the Tibet phase. The crystal structure of this pigment phase could not be resolved but was somehow similar to Prussian blue that may not have been used in the fourteenth century (see Chapter 7).

The *tsakali* are used in initiation rituals to empower neophytes in the particular domain of religion they represent. Once a tool for passing down knowledge from master to student, the set may have been designed and produced specifically for a person at a particular level of spirituality. It is also possible that certain cards were produced later as the learning process continued. Thus, it is obvious that the story of the production and usage of this heritage object is more complicated. This spurred the need for a cross-disciplinary analysis of the set, including undertaking the independ-

ent method such as radiocarbon dating, which would help to narrow down the time period in which the *tsakali* were produced.



Figs 1a–b: (a) Tsakali O, depicting a *bum pa* vase, and (b) Tsakali D, showing the figure of gSang ba ngang ring.

Considering the above-mentioned hints, the object of our study is a part of the cultural heritage of Tibet. This is why the possibilities for sampling are very limited, and only the AMS method can be considered (smaller samples are required). Because ^{14}C is a destructive method, for a historical object such as this, we decided

to start our research with just one sample, and postponed dating any other cards until we received the results obtained by the other methods. Moreover, the sampling was discussed with the owner of the object, whose permission was obtained. All the cards are cut to the same dimensions (9.4 cm in width × 20.2 cm in height) and made of paper; however, the numbering added later on suggests that we are dealing with at least two different sets within this collection. Each card bears a number or letter indicating the sequence of the card in the collection. The paper they are made of also consists of two types, suggesting that different papermaking sieves were used in its production. This is why the samples considered for ^{14}C analysis were selected from two cards bearing different features.

The first sample was taken from a damaged area of *Tsakali* O, depicting a *bum pa* vase; later, a second sample was taken from *Tsakali* D, showing the figure of *gSang ba ngang ring* (Figs 1a–b). The selection of sample locations was conditioned by (1) no materials other than paper being present, (2) no damage, like fungi spores or other marks of degradation, being visible.

2 Dating paper by radiocarbon method

Radiocarbon dating is applicable to manuscripts composed of organic materials; using milligram-sized samples, it has been used to estimate the age of books as well. Though impractical in its early decades, when as many as several grams of carbon were needed for ^{14}C measurement, the radiocarbon method became a more convenient tool for dating paper after the AMS technique was invented, requiring carbon amounts of 1 mg or even less. It is independent of other methods, objective, and the only truly quantitative method for dating organic materials. However, as many scholars have pointed out, this technique alone usually cannot resolve issues of authenticity or provide precise dating.

The calculations of the $^{14}\text{C}/^{12}\text{C}$ ratio in organic materials produce ages in radiocarbon years, which are not identical with calendar years (as the mentioned $^{14}\text{C}/^{12}\text{C}$ ratio has not been constant historically). The study of tree rings (as a sequence of securely dated samples) has allowed us to produce a so-called ‘calibration curve’ that relates calendar dates to radiocarbon ages.¹ Using this curve, one can calibrate radiocarbon age, i.e. derive a calendar date from the results of ^{14}C measurement. As seen from the wiggly shape of the calibration curve shown in Figs 2a–b, the calibrated date (being the best estimate of calendar date) usual-

¹ The most recent calibration curve has been published by Reimer et al. 2020.

ly has a probability distribution of complex shape and – even if ^{14}C age is determined with a 1-sigma uncertainty of ± 30 yr – may encompass a time interval as wide as fifty to three hundred years, depending on the date itself. There exist various internationally-used software for calibrating ^{14}C ages, one of the most popular being OxCal.²

However, the precision of the measurement does not depend only on the object's time period or the calibration curve. It is very important to understand the material composition of the sample tested. Paper as writing support, with all its components, is a very complex and unique material, which is why it is difficult to understand at the molecular level, especially considering that a large number of its components undergo both technological and deterioration processes occurring at different stages and times, as well as the influence of various environmental factors. Thus, we have to clearly understand which point of the heritage object's life we are dating.

^{14}C analysis reveals only the period of formation of the plant cellulose molecules in the paper's fibres, and not the period of the paper's manufacture; the papermaking process will sometimes blend fibres from a wide variety of original sources, harvested at different times. An obvious obstacle to the accurate ^{14}C dating of paper industrially produced from the trunks of trees that had grown for decades is that ^{14}C signal of each tree ring represents the time of its formation (and not that of cutting the tree), so the ^{14}C signature of paper is an average of radio-carbon signals from many years, with individual years being unknown. In this respect, however, the age of the cellulose in the *tsakali* paper truly represents the time of the paper's manufacture, as it was made from the phloem of living plants, i.e. from the carbon-bearing tissue assimilated in the year of harvesting, or only very shortly before. Other substances, such as dyes or fillers, may have been added when processing the paper before writing, and organic materials may be found in pigments and other substances applied later on. These may contaminate samples with carbon of lower or higher ^{14}C signatures, which also may make the results of ^{14}C dating disputable.

3 Methods: A short overview

A sample of paper submitted to ^{14}C dating contains carbon in various chemical fractions, potentially of different ages and different ^{14}C isotopic signatures. Thus,

² Bronk Ramsey 2009.

the crucial goal of chemical pretreatment is to extract the fraction that is most representative of the true time of paper production. The remaining steps of the ^{14}C dating procedure, i.e. deriving pure carbon from this fraction and making AMS $^{14}\text{C}/^{12}\text{C}$ measurements from it, are more or less common to all AMS radiocarbon laboratories.³

In general, the paper fraction most suitable for dating is cellulose, which constitutes the walls of wood cells; after its formation, it is extremely resistant to the exchange of carbon inside the plant of origin (e.g. inside the tree trunk) and – after the tree is cut and paper produced – with the ambient environment.⁴ Besides cellulose, other organic fractions of wood are lignins, waxes and resins, which are potentially mobile in plants and to some degree also in the environment. The carbon pool produced in the ancient paper (containing also that of dyes and fillers, mostly contemporary with the time of paper production) may then, during the long period between its production and today, be modified due to the absorption of fulvic and humic acids (organic fractions mobile in humic environments) and eventual precipitation of carbonates. Ultimately, sample material may be contaminated with organic impregnates/preservatives and/or simply with fats deposited during its handling by humans.

An extensive review of chemical pretreatment protocols used for AMS ^{14}C dating⁵ has recommended the method coded as VV for paper, consisting of sequential treatment with 1M (c. 4%) HCl (20°C–80°C) to remove fulvic acids and carbonates; 0.2 M (c. 1%) NaOH (20°C–80°) to remove humic acids; and another treatment with 1M HCl to remove the carbon absorbed from atmospheric CO_2 during the treatment with NaOH, with temperatures adjusted individually in order to prevent the complete dissolution and loss of the sample material.

Referring to the main sources of paper contamination, examples of successful ^{14}C dating of ancient paper describe several versions of the chemical treatment applied. In the ^{14}C dating of the *miidera-gire* Japanese calligraphy sheets, dated between 1400 and 1200 years old, Hirotaka Oda treated the paper with a procedure very similar to that of the VV protocol outlined by Fiona Brock.⁶ More rigorous processing – in which the VV protocol was preceded by treatment with organic solvents to remove contamination from oils and waxes – was applied in dating manuscripts between 1200 and 200 years old from the Central Library of the Uni-

3 See Goslar, Czernik and Goslar 2004 for an example.

4 See e.g. Němec et al. 2010.

5 Brock et al. 2010.

6 Oda et al. 2011; Brock et al. 2010.

versity of Tehran.⁷ On the other hand, Buddhist sutras from the twelfth to fourteenth centuries⁸ were dated by measuring ¹⁴C in the cellulose extracted from these materials.

4 ¹⁴C dating of *tsakali* paper

The ¹⁴C dating of the *tsakali* paper was performed at the Poznań Radiocarbon Laboratory.⁹ After the chemical pretreatment of a sample, combustion of residue to CO₂, reduction of CO₂ to graphite, and AMS ¹⁴C measurement of the graphite, the conventional ¹⁴C age of the sample was calculated,¹⁰ then calibrated against INTCAL20¹¹ using OxCal ver. 4.4.2.¹² The determined ¹⁴C ages and calibrated dates of the analysed samples are presented in Table 1.

The first sample of Tsakali 0 (see Table 1) was chemically processed with a weak version of the VV protocol (with every step at room temperature; see the section above), preceded with overnight subsequent soakings in acetone, alcohol (2-isopropanol) and water, and followed by a thirty-minute treatment with 2.5% NaClO₂+HCl (20°C). In general, acetone and alcohol are the solvents applied to remove contamination by organic impregnates/preservatives (introduced e.g. for maintenance in a museum); however, the *tsakali* have never been maintained in such a way, so here the acetone/alcohol treatment was applied just to remove the modern fats deposited during handling by humans. Further, treatment with NaClO₂ is generally applied in the ¹⁴C dating of wood¹³ in order to remove potentially mobile fractions such as lignins, resins and waxes. In order to avoid a complete loss of the sample material, all the treatments above were applied at room temperature, and the total loss appeared small: of 14.0 mg of raw sample, as much as 8.2 mg of material ultimately remained.

The calibrated ¹⁴C date of Tsakali 0, which is the second half of the fifteenth century at the oldest, is younger than its stylistically-based association with the fourteenth century suggests (Figs 2a–b). In light of this, and of the rather small

⁷ Aghaei et al. 2023.

⁸ Oda, Nakamura and Furukawa 1998.

⁹ Goslar, Czernik and Goslar 2004.

¹⁰ According to Stuiver and Polach 1977.

¹¹ Reimer et al. 2020.

¹² Bronk Ramsey 2020.

¹³ Brock et al. 2010.

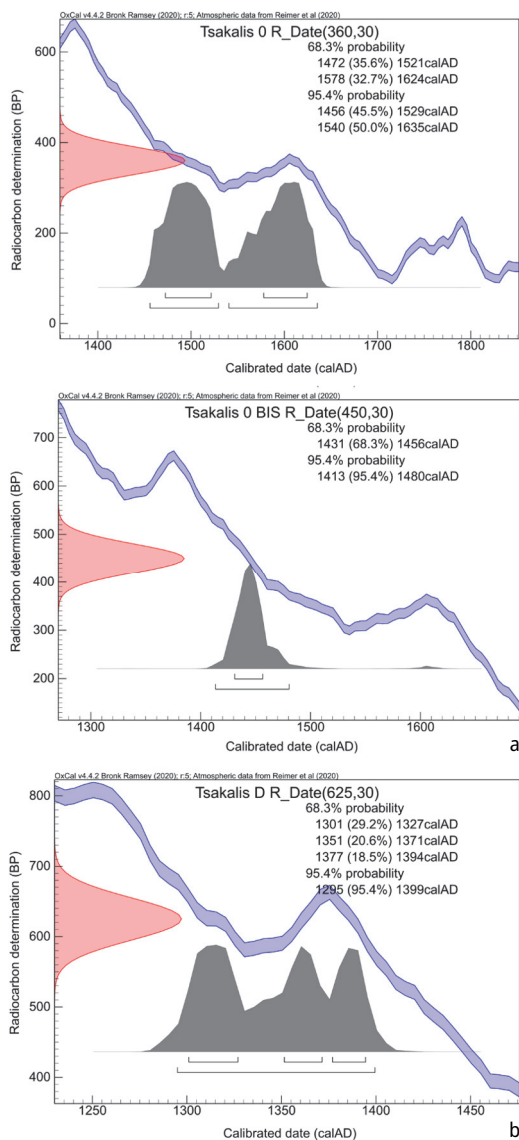
loss of material in the weak VV treatment, we decided to date another subsample (called Tsakali 0 BIS), applying a much stronger process of cellulose extraction. In detail, the sample was subsequently treated with 1M NaOH (80°C, overnight); 1M HCl (80°C, 1h); 1M NaOH (80°C, 1.5h; the step was repeated until no more colouration occurred); 1M HCl (80°C, 1h); 5% NaClO₂+HCl (pH=2, 80°C, 2h; the step was repeated until a white colour was obtained from the sample); and 5% NaClO₂ (pH=2, 20°C, 15m in an ultrasonic bath). The loss of material in this process – only 1.25 mg from the initial mass of 13.1 mg remained – was much bigger than in the weak VV attempt, so we can be sure that for Tsakali 0 BIS, the contamination potentially altering the ¹⁴C age has been removed much more effectively.

A difference between ¹⁴C ages of Tsakali 0 and Tsakali 0 BIS (360±30 BP vs 450±30 BP), significant at a level of 5%, suggests that the first dating result was slightly inaccurate due to the younger contamination not being fully removed by the weak VV processing. Nevertheless, the card Tsakali 0 appears to date from the mid fifteenth century, and is therefore younger than its stylistically-based association (Figs 2a–b).

The same process of cellulose extraction from the sample of Tsakali D had an even lower yield (0.55 mg remained from 8.4 mg of raw material); this sample was ¹⁴C dated to 625±30 BP, indicating any time within the fourteenth century. So we can be nearly sure that the two *tsakali* (0 and D) were manufactured at different times, with Tsakali 0 having been produced at least fifty years after Tsakali D (Figs 2a–b).

Table 1: Results of the radiocarbon analysis of *tsakali* paper presented in this study.

Sample name	Procedure	Raw sample (mg)	After treatment (mg)	To combustion (mg)	After combustion (mg)	Lab no. Poz-	¹⁴ C age	Calibrated date (68.3%)	Calibrated date (95.4%)
Tsakali 0	Ac/Alc + VV + bleaching	14.0	8.2	2.5	1.08	153645	360±30 BP	1472–1521 CE 1578–1624 CE	1456–1529 CE 1540–1635 CE
Tsakali 0 BIS	Ac/Alc + cellulose	13.1	1.25	1.25	0.76	162877	450±30 BP	1431–1456 CE	1413–1480 CE
Tsakali D	cellulose	8.4	0.55	0.55	0.26	167393	625±30 BP	1301–1327 CE 1351–1371 CE 1377–1394 CE	1295–1399 CE



Figs 2a–b: Results of the calibration of ^{14}C ages determined for three samples of paper from (a) Tsakali 0 (two samples) and (b) Tsakali D (one sample). The pink bell-shaped curves on the y-axes represent probability distributions of the radiocarbon age, whereas the grey shapes on the x-axes are the probability distributions of the calibrated dates. The sub-intervals making up the 68.3% and 95.5% confidence intervals of the calibrated dates are displayed in the square brackets below. The thick blue bands represent fragments of the ^{14}C calibration curve.