THE ERLANGEN AMS FACILITY AND ITS APPLICATIONS IN ^{14}C SEDIMENT AND BONE DATING

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ABSTRACT. We report here on the radiocarbon dating of sediment samples from Bavaria using the Erlangen accelerator mass spectrometry facility. The absolute time calibration of different sediment profiles, together with pollen analyses, should establish a better chronology of climate and vegetation during Holocene in Bavaria. For an enhanced reliability of sediment dating, we measured different fractions such as bulk sediments, pollen grains, macrofossils and humic acids. For these fraction, we describe the separation methods and conversion to sputter targets. Furthermore, we discuss the sample preparation for the dating of bones and present some results.

INTRODUCTION

The Erlangen accelerator mass spectrometry (AMS) facility (Kretschmer *et al.* 1997a), based on an EN tandem accelerator, is now routinely used for radiocarbon dating with an annual throughput of *ca.* 400 unknown samples. The accelerator is a shared facility with AMS using *ca.* 20% of the available beam time. The analyzing system is also designed for heavier isotopes, as has been demonstrated using the setup for quick detection of ^{90}Sr (Arslan *et al.* 1994, 1995). In this contribution, we describe the experimental setup, and the sample preparation for different fractions of peat sediments and bones. For one continuous sediment core covering the time range of the last 15,000 yr, we compare the results for bulk sediment, macrofossils >100 μm, and pollen grains between 20 and 100 μm. Finally, we report on preliminary tests for bone dating.

Experiment Preparation

The AMS facility consists of a high-current sputter ion source, a 90° injection magnet with fast isotope switching, an EN tandem accelerator, a 15° electrostatic deflector, a 55° analyzing magnet (for ^{14}C), a 120° magnetic split pole spectrometer (for heavier ions) and a ΔE-E gas detector. The sputter ion source (Höpfl *et al.* 1992), equipped with a spherical ionizer and a cassette for 50 samples, is fully computer controlled and delivers $^{12}C^-$ currents of up to 150 μA at an energy of 55 keV. The particle transmission through the facility amounts to 80%, taking into account the charge distribution in the high-voltage terminal. Thus, even with conservative ion source conditions of 25 μA $^{12}C^-$ current, a ^{14}C count rate of 100 Hz can be obtained for an ANU sucrose calibration sample. Machine background, determined with graphite samples, is measured at 0.07 pMC, corresponding to an apparent age of 58,000 yr. The measurements are made in turns of 1-min runs, allowing an online control of the system *via* the particle transmission and the isotope ratios. In the routine sequence of AMS measurements the quality of the whole facility is first checked with calibrated samples (ANU sucrose, wood from 1860 AD, 23.05 pMC IAEA C5, graphite) that have been treated in the same manner as the unknown samples. Then two to three unknown samples are measured before another calibrated sample is used. We have established accuracies of better than 1% this way. For the mass fractionation correction, we have used both standard and $^{13}\delta$ values measured in a conventional mass spectrometer.

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Sample Preparation

The sediment cores (Kretschmer *et al.* 1997b) were taken from different Bavarian bog sites that developed from ancient lakes and fens. Since not all carbon-containing components of the sediment are representative for the age of the investigated layer, a special chemical treatment must be performed and single components must be dated separately. In the so-called AAA chemical pre-treatment, the two major components that may obscure the ^{14}C results are removed: 1) carbonates arising from the erosion of limestone are removed by heating the material with HCl, and 2) humic acid that may be younger due to its high mobility is removed by heating it together with NaOH. The second procedure is repeated until the brown color of the solution vanishes. Finally, the pretreatment is finished by heating in HCl, washing in deionized water and drying the remaining material in an oven.

The organic residue is called bulk sediment, since up to now no separation due to the size of the objects has been performed, and because it represents a mixture of the remains of water plants, algae, pollen and different macrofossils. This pretreated bulk sediment is now converted to a sputter target, which enables the formation of a high-current negative-carbon ion beam. It is first converted to carbon dioxide by heating it at 900°C in an evacuated quartz tube together with copper oxide and silver wool, where the latter is used to remove possible sulfur contamination. After a slow cooling, the tube is cracked in the reduction facility, where graphitization takes place by heating an appropriate mixture of hydrogen and carbon dioxide at 625°C with ion powder of 10 μm as a catalyst. Details of the reduction procedure are described elsewhere (Kretschmer *et al.* 1997a).

Since it is the aim of our project to deduce the vegetation history from the pollen distribution in the sediment core, direct dating of the pollen is highly desirable. For the extraction of the pollen grains from the sediment, we mainly follow a procedure described by Brown *et al.* (1992) and shown schematically in Figure 1. The material is heated in 1N NaOH at 80°C for deflocculation and the removal of humic acids. Then it is sieved with a 100-μm nylon mesh. The residue is investigated for single macrofossils and then treated like the bulk sediments described above. The filtrate is repeatedly

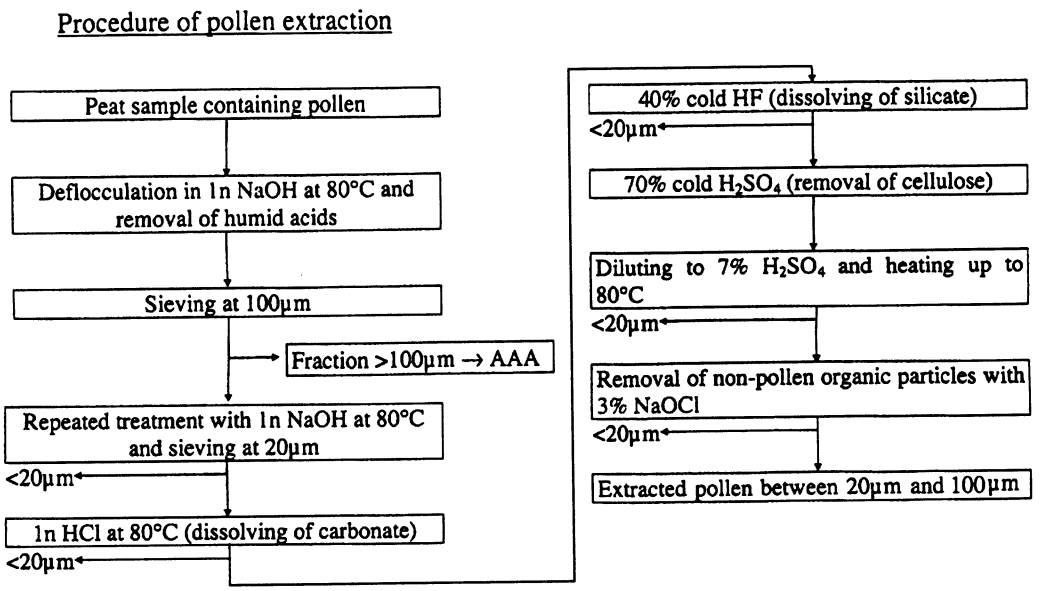

Fig. 1. Extraction of pollen grains from sediment samples

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heated with 1N NaOH, followed by 1N HCl for the removal of carbonates. Silicates with <100 μm are removed by ultra centrifugation and by dissolving in 40% cold HF. The cellulose is removed with H_2SO_4, and finally, for the deflocculation of amorphous organic material, a treatment with NaOCl is performed.

After each step the dissolved material is separated from the pollen grains by sieving with a 20-μm nylon mesh. The efficiency of this separation method is finally checked under a microscope. The conversion to sputter targets *via* vacuum oxidation and catalyzed reduction is done in the usual manner described above. Depending on the pollen density in the sediment layers, the amount of remaining carbon varies between 50 and 500 μg. For a minimization of contamination with modern carbon background, the reduction of these samples is performed in a recently built reduction apparatus with a volume of only 2.9 cm^3 (Kretschmer *et al.* 1997a). The background for sub-mg graphite samples (Fig. 2) is mass-dependent and has to be taken into account for the pollen measurements.

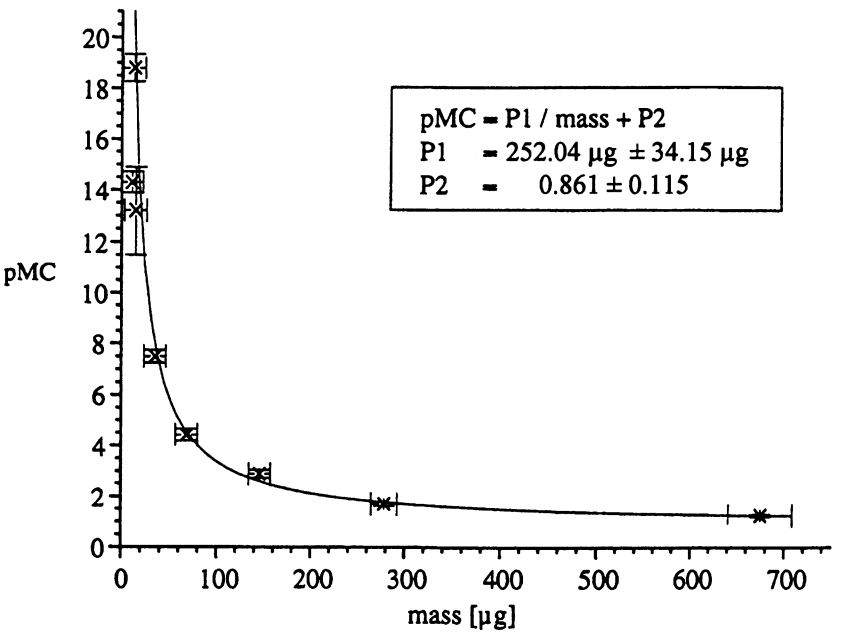

Fig. 2. Background for sub-mg graphite samples

For the dating of bones, we follow a modified procedure proposed by R. Longin (1971), as shown schematically in Figure 3. The method is based on the removal of the inorganic fraction and the extraction of collagen. In an ultrasonic treatment, the bone is cleaned with deionized water. Then the carbonates can be removed in two alternative ways: 1) either the dried and ground bone, or 2) the complete bone is treated with 0.5–1 N HCl. Grinding accelerates the procedure, but if the bone contains only a small amount of collagen, it may be lost. In the next step, humic acids are dissolved with 0.25–1 N NaOH, and finally the collagen is extracted by dissolving the residues in acidic water (pH = 1–3) at 58°C for 16 h. Remaining insoluble residues are separated by centrifugation and can be dated for a comparison. By drying the solution at 80°C, all collagen can be obtained in form of gelatin. It is also possible to get rid of some remaining contamination by an additional ultra-spin-macrofiltration. In this way, the gelatin fraction with molecule masses >30 kD can be extracted and then dried as described above. The residues are washed with deionized water after each step.

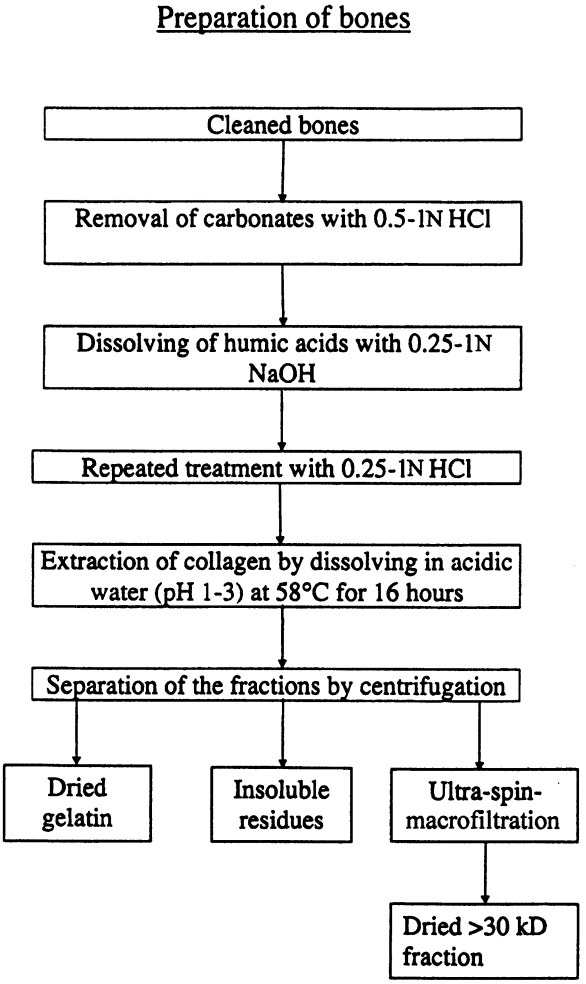

Fig. 3. Preparation of bones for ^{14}C dating

Sediment Samples from Bavaria

We investigated several sediment cores from southern Bavaria. In this paper we present the methodical study of a core from the Eggstätt Fen northwest of Lake Chiemsee, which has been a kettle hole with no inflow or outflow of water. Therefore, a rather regular sedimentation rate is expected. The bog is now covered by a 0.5-m thick layer of recent humus followed by a 3.50-m thick layer of water. Therefore, the sediment core extends from 4 m to 10 m below ground level. The results of our ^{14}C dating are shown in Figures 4a–c for bulk sediment, pollen grains and the >100-μm fraction, respectively. As expected, the sediment growth rate is rather constant. All three fractions show an astonishing agreement in their absolute dates, except for the lowest layer close to 10 m, consisting mainly of lake marl. At this depth, the bulk sediment is *ca.* 1500 yr older than the pollen grains, which may be due to the hard-water effect. At a depth of 5.80 m to 5.90 m, we dated a seed and humic acids. Both are in agreement with the results for the 100-μm fraction. In summary, for this site the overall agreement for the different components increases the reliability of results for this sediment core. However, the growth conditions of fen sites are not always that favorable. Another sediment core, from the Oberau Fen, contained many small pieces of wood originating mainly from roots. As the

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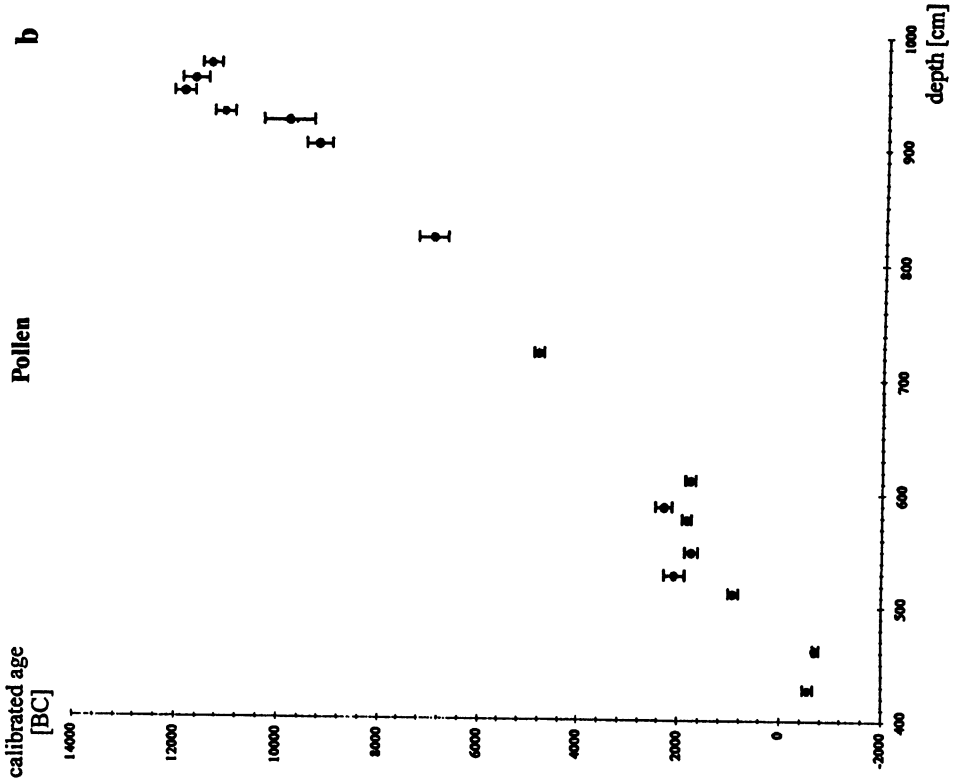

Fig. 4b. See Fig 4c, following page.

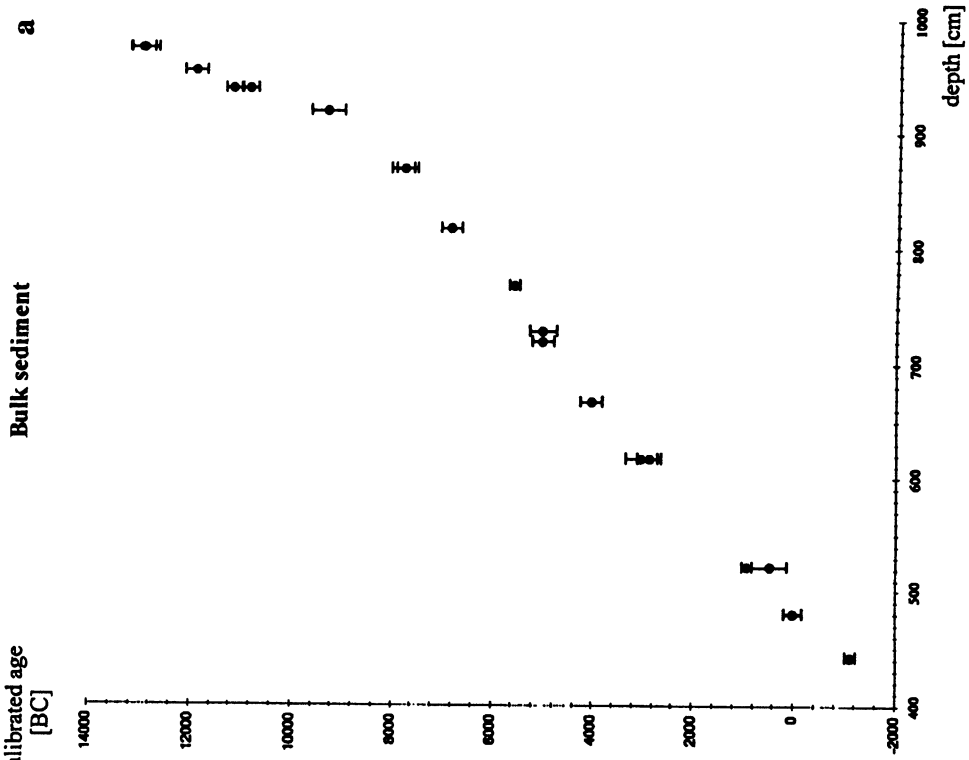

Fig. 4a. See Fig 4c, following page.

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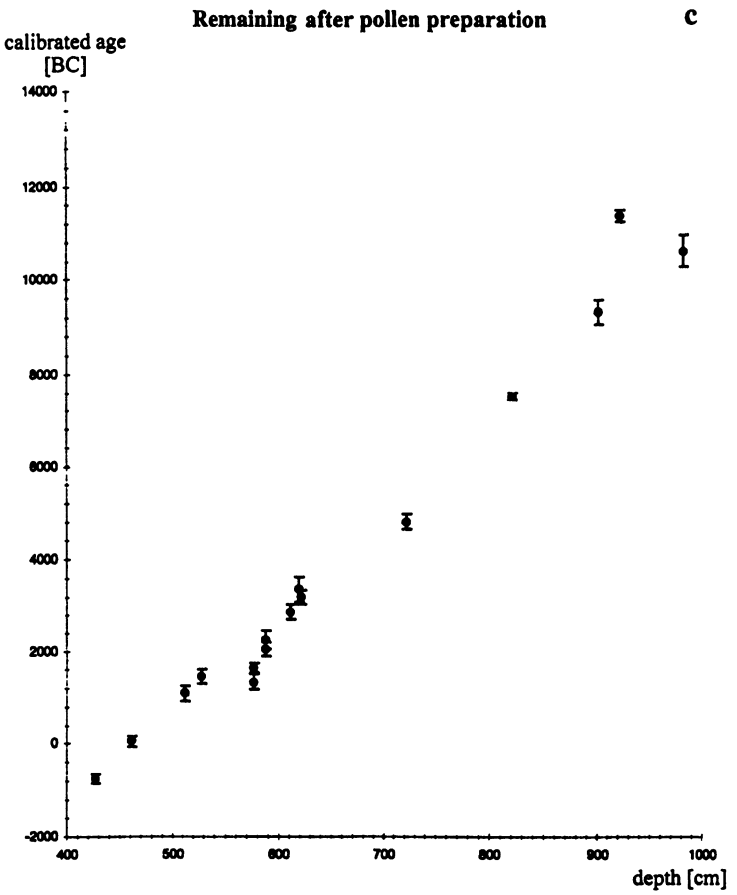


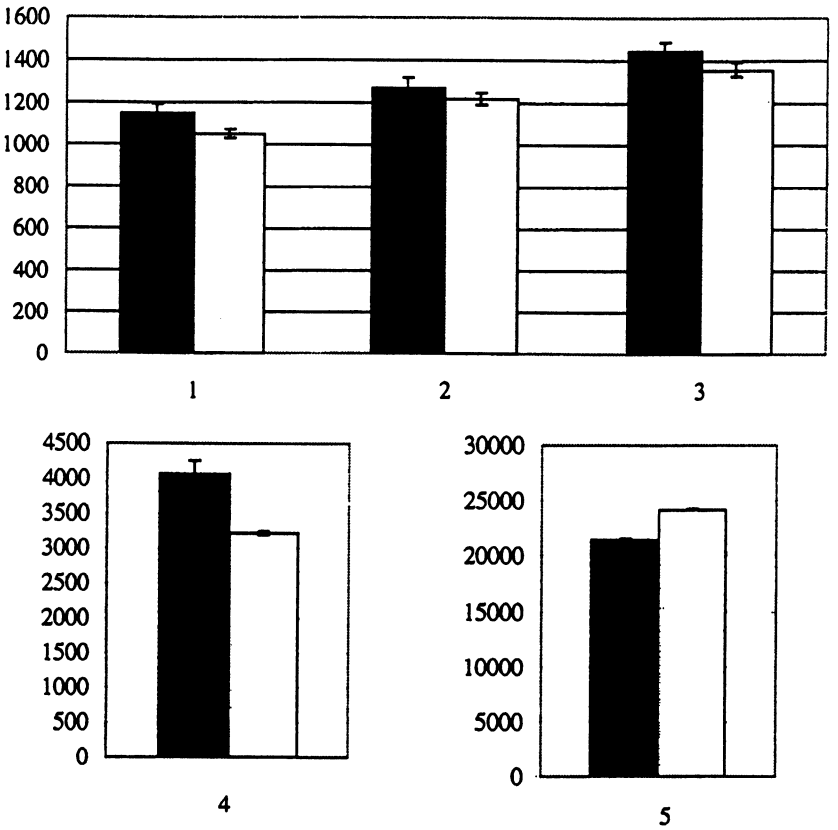
Fig. 4. Calibrated age *vs.* sediment depth for the Eggstätt sediment core. a: bulk sediments; b: pollen grains (20–100 μm); c: fraction >100 μm.

detailed investigation of the vegetation history of this fen showed, there were dry periods, favoring the growth of trees at this site. Because of this, both the dating of wood and of bulk sediment were obscured by the roots penetrating into the deeper layers of the fen. Therefore, we consider the pollen dates for this site representative for the corresponding layer, and thus most reliable.

Dating of Bones

In most cases, for bone dating we used collagen that was filtered by a 100-μm mesh and then dried to gelatin. For the dates of bones that had already been measured at the Groningen facility, we obtained with this fraction agreement within 2 σ for three samples and disagreement for two samples. The following predated samples were measured: two samples from Ireland (Chancellorsland A 10 and Clonmacnoise SCe burial), one from a pleniglacial settlement in Russia (Khotylevo II/ cultural layer), and one from Norexy, France (Norexy la fin tout chien 29). The results are shown in Figure 5. The disagreement of the sample from Chancellorsland could be due to the very small amount of extracted collagen resulting in only 46 μg carbon.

As shown in Figure 2, the background for samples of this size is strongly mass dependent and may have been overestimated in this case. The Kotylevo II sample was abundant with collagen and contained a large amount of carbonate that had been removed by a treatment with HCl for 24 d. The dis-



Graph no.	Sample	Dating facility	Date
1	Platen 2 E4-7	Groningen (right bar)	1050 ± 20 BP
		Erlangen (left bar)	1150 ± 44 BP
2	Clonmacnoise SCe burial	Groningen (right bar)	1120 ± 30 BP
		Erlangen (left bar)	1273 ± 46 BP
3	Norexy la fin tout chien 29	Groningen (right bar)	1360 ± 30 BP
		Erlangen (left bar)	1441 ± 42 BP
4	Chancellorsland A 10	Groningen (right bar)	3220 ± 30 BP
		Erlangen (left bar)	4067 ± 191 BP
5	Khotylevo II/cultural layer	Groningen (right bar)	24,220 ± 110 BP
		Erlangen (left bar)	21,423 ± 180 BP

Fig. 5. Comparison of bone-dating results from Erlangen (black bars) and Groningen (white bars)

agreement for this sample could be caused by a contamination with <2 pMC during the chemical processing of the bone, or by an incomplete removal of the carbonate in Groningen.

For the unknown samples we got results within the expected age range. The rib of a wolf, found in the Zoolithen cave near Erlangen, was dated to 24,330 ± 370 BP; bones from Reckenbühl were dated to 982 BC ± 140 a and the dating result for bones from a Roman port at the river Danube was 91 AD

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± 125 a, the error corresponding to 2 σ. For bones from this Roman excavation, we tested the ultra-spin-macrofiltration mentioned above. The >30 kD fraction was slightly older than the dried gelatin, which may be an indication that younger impurities are <30 kD.

Conclusion

It has been shown that different fractions of sediment samples can be dated separately, which increases the reliability of the measurement. For bone dating, collagen has been extracted and converted to a sputter target. Preliminary tests with predated and unknown bone samples of ages up to 25,000 yr exhibit promising results.

Acknowledgment

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