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MULTIPLE DATING OF A LONG FLOWSTONE PROFILE*

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ABSTRACT. Dense speleothem samples are considered as closed systems and are, therefore, possibilities for any dating method. Four dating methods (^{14}C, U/Th, paleomagnetism, and electron spin resonance = ESR) were used for samples up to 1,000,000 yr old and taken along a vertical flowstone profile in the Heggen cave in West Germany. Also $\delta^{18}O$ and $\delta^{13}C$ analyses were carried out.

The reliability of the results of each method is dependent on the diagenetic processes that took place during the complex growth history of the flowstone. Speleothem growth was interrupted during glacial periods. During interglacial periods, at least the stalagmite growth rate was greater by one order of magnitude than during interstadial periods. During the periods of low interstadial growth rate various processes might have changed the ^{14}C, ^{18}O, and ^{13}C concentrations, leaching might have removed uranium, recrystallization might have moved thorium several centimeters, and increased content of radon in the cave might have exaggerated the accumulated dose (AD) at the speleothem surface. As a result, ^{14}C ages may be too small and U/Th as well as ESR data may be too large.

INTRODUCTION

Long-term paleontologic and isotopic records from pelagic marine sediments are the basis of our present knowledge of the global climate during the last million years (Shackleton & Opdyke, 1973). Applying the Milankovitch theory the time scale has been "tuned" to an accuracy of ±2000 yr (Hays, Imbrie & Shackleton, 1976). In order to recognize the causes of paleoclimatic changes, variations within specific continental climatic regions must be studied. But, apart from continental ice there is no other natural long-term climatic record reflecting the multiple interglacial/glacial transitions. Lacustrine sediments are formed only during wet or interglacial and interstadial periods but might have been eroded during arid or glacial periods. Moreover, lacustrine sediments show a delayed response to climatic changes due to interaction with groundwater. Although speleothems are formed exclusively during interglacial and interstadial periods (Franke, 1951; Geyh & Franke, 1970), a vertical flowstone profile grown during one million years was a challenge for a paleoclimatic study.

SITE OF STUDY

The Heggen cave in northwest Germany (maximum length, 30m; height, 4m) contains a flowstone block 120cm thick and ca 2m in diameter. The roof of the cave consists of ca 4m of limestone overlain by soil covered with grass. The cave was not open until ca 100 yr ago. A cross-section was cut through the block ca 40 years ago, which now offers rather ideal conditions for profile sampling.

PETROGRAPHY OF THE SITE

The flowstone which is 120cm thick, is highly stratified with different colored layers (Fig 1). Clay minerals and iron hydroxides enrich the dark brown zones, a few of which might have been formed during deposition. Many of the light brown layers may have been formed as a result of recrys-

* *Editor's note:* See Radiocarbon, v 28, no 3, 1986, for a discussion on this article.

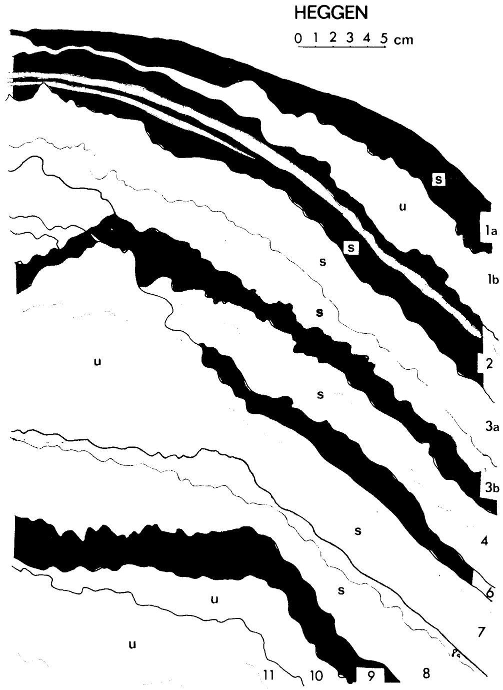

Fig 1. A vertical flowstone profile in the Heggen cave. Dots represent shades of brown in nature; s denotes stratified layers; u stands for uniform, coarse crystalline zones; the hatched zones are oriented, transparent calcite crystals.

tallization. Calcite crystals up to a few centimeters long pushed impurities upward through many deposition layers of millimeter thickness or less. Hence, recrystallization layers often cut through deposition layers visible only in thin section. No annual layers seem to be present. Both types of brown layers may be either uniform or stratified.

Most of the flowstone consists of white, yellow, or transparent, mostly coarse crystalline layers. In some parts, the compound of the crystals is very soft and can be broken into single crystals with the fingers.

The numbering of the layers (Fig 1) is based on the notation of the initial geomagnetic study and does not take petrographic and sedimentologic aspects into account. The layers used for geochronologic analyses (1 to 2cm thick) are described in Table 1. An assumed sedimentation rate of 1cm/1000 yr for Holocene flowstone (Geyh & Franke, 1970) suggested an age of Pleistocene to Holocene transition in a few sharp boundaries of the top 10cm, but this proved incorrect, as shown below.

GEOCHRONOLOGIC INVESTIGATIONS

The significance of any paleoclimatic information depends upon the validity of its chronologic classification. We have used various dating meth-

TABLE 1
Results of the geochronologic investigations

Layer	Depth (cm)	Layer	Conventional ^{14}C age (bp)	U/Th age (ka)	ESR age (ka)	AD (krad)
1a	0.5 – 1	Dark brown, stratified	3135 ± 60	3.1 ± 1.1		
			3560 ± 45	3.7 ± 1.9	43–72	ca 1.0
1b	– 2.3	White, coarse crystals	7330 ± 80	4.9 ± 2.2	43	ca 0.9
2	– 3.5	Dark brown, stratified	8430 ± 85	5.9 ± 1.0	63	ca 1.5
3a	– 5.5	White, center of crystals	9600 ± 130	9.0 ± 0.6	118	ca 4.2
		White, surface of crystals	9255 ± 125	13.1 ± 0.7	—	—
3a		Coarse, white crystals	11,355 ± 190	20.0 ± 2.0	—	—
3b	– 8.0	Light brown, stratified	13,330 ± 165	92.1 ± 5.1	133	ca 4.4
3–4		White and brown	—	91.0 ± 7.0	120	ca 3.3
3–4		White and brown	—	100 ± 8.0	—	—
4	– 10.0	Coarse, yellow crystals	28,720 ± 2250	—	135	ca 4.2
5/6	– 12.0	Dark brown, stratified	39,000 ± 1870	343	225	ca 6.5
7		Coarse, white crystals	36,390 ± 1260	140 ± 40	—	—
7a		Coarse, white crystals	—	171 ± 14	264	6.6
7b		Coarse, white crystals	—	208 ± 36	263	11.4
8		Brown & yellow crystalline	—	—	368	10.9
9		Dark brown, stratified	—	300 ± 76	472	15.0
10		Uniform, white crystals	—	192 ± 25	—	—
11		Uniform, white crystals	—	237 ± 29	343	9.3
12		Brown, stratified	—	265 ± 40	345	9.0

ods and the results of other studies:

- paleomagnetic dating (Krumsiek, pers commun)
- ^{14}C dating
- $^{234}U/^{230}Th$ dating
- ESR analysis (Grün, 1985)
- stable oxygen and carbon isotope analyses.

The raw data for these analyses are compiled in Table 1 or shown in Figure 3.

Paleomagnetic dating

The top 70cm of the flowstone profile has a normal magnetic orientation; below 70cm, from Layer 18 downwards, the magnetic orientation is reversed. Hence, the contact zone seems to be related to the Bruhnes/Matuyama reversal at 710 ka.

Conventional ^{14}C data

Conventional ^{14}C data (Table 1) were obtained from samples ca 2cm thick and represent an average time range of 1000–2000 yr; 1000 yr or more (Geyh, 1970) must be subtracted from the conventional ^{14}C data due to the reservoir effect.

Applying a linear least square fit to the data below 10,000 yr, the Holocene growth rate was 12.5mm/1000 yr until 7000 yr and later 2.9mm/yr. The ^{14}C time scale is shifted by – 1700 yr. This corresponds to an initial ^{14}C

content of 81% of modern. However, this value depends on the soil cover, which may have changed during the past.

The ^{14}C data indicate that the deposition rate was greater at the beginning of the Holocene than at the present. With the mean growth rate mentioned above, the Holocene/Pleistocene transition should be found within the top 7.1cm, *ie,* in Layer 3b.

The ^{14}C ages of 28,700 to 39,000 yr bp for Layers 4, 6, and 7 do not provide any clues about whether the flowstone was formed or preserved during interstadial periods. Studies on similarly old flowstone in other European caves have established that contamination of up to 4.4% of modern, corresponding to a ^{14}C age of 25,000 yr, may occur. This can be caused by isotopic exchange or more probably by precipitation of young carbonate in pores or fissures.

A contamination test was made on Layer 3a, for which both outer and inner parts of coarse-grained calcite crystals several millimeters long were dated. The maximum contamination amounts to 1.4% of modern only.

$^{234}U/^{230}Th$ data

Most of the U/Th and ^{14}C data were determined using the same samples. The U/Th ages include a correction for detrital thorium using an initial $^{230}Th/^{232}Th$ activity ratio of 1, the center of the common range. The uranium concentrations vary within the layers between 170 and 360ppb (Grün, 1985).

Down to Layer 3a, the U/Th ages agree quite well with the ^{14}C ages. The difference of 4100 yr in the U/Th ages between the outer and inner fractions of the calcite crystals of Sample 3a may be due to a greater concentration of detrital thorium in the crystal surfaces (which should be corrected for) or to open system problems, eg, recrystallization. This last mentioned effect is obvious for Sample 3b, which may be a mixture of 80% Holocene (3a) and 20% Eemian flowstone, on the basis of the ^{14}C content, assuming interstadial flowstone was not present.

A linear least square fit of the U/Th data yields a growth rate of 7.1mm/1000 yr and an intercept of 2560 yr. The Holocene boundary should be within the lower third of Layer 3b, in reasonable agreement with the results of the ^{14}C analysis.

The U/Th data of the older samples below Layer 5/6 have a wide scatter with an increasing trend. The brown samples (Layers 5/6, 9) above white or yellow, coarse-grained crystalline layers always yielded higher U/Th ages than the latter. An explanation may be that the growing calcite crystals pushed impurities, including thorium, upward and formed the brown layers.

If such a process occurred, it would also be impossible to decide, on the basis of U/Th data, whether interstadial flowstone was formed or even preserved and where the boundaries of the glacial/interglacial transitions can be found.

ESR data

The ESR determinations of the accumulated dose (AD) (Grün, 1985) for three vertical profiles have a wide scatter (Fig 2). Only one shows an

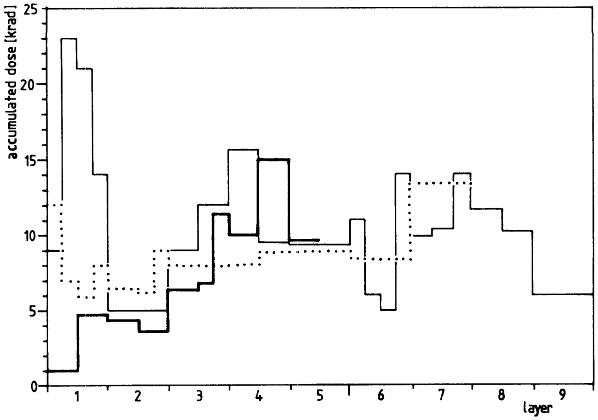

Fig 2. Scattering AD data from three vertical profiles in the Heggen flowstone (Grün, 1985)

increasing AD without any indication of a particular petrographic situation. The apparent stepwise increase of the AD in Layers 1b–2, 2–3a, 4–5/6, and 7–8 does not coincide with the boundaries reflected by the ^{14}C and U/Th data.

One explanation is provided by the results of the first international ESR comparison project (Hennig, Geyh & Grün, 1985). The minimum interlaboratory reproducibility was ±25% and went up ≥±100%. Therefore, ESR ages of 40 ka for Holocene samples are not surprising. On the other hand, increased dose rates during glacial periods resulting from a high radon concentration when the cave was closed by ice could be another explanation.

Most of the samples deeper than Layer 2 yielded ESR ages with a range of 200 to 400 ka without an obvious trend towards an increase with depth. This may be partly due to recrystallization. Another reason may be that the sample thickness of 2cm was too large to obtain a good time resolution. In addition, if even a small quantity of fossil limestone is present ESR dates appear too large (Debenham & Aitken, 1984). Moreover, there are still many other unsolved problems with the ESR method (Grün, 1985). Last but not least, the high AD values of the deepest samples, which correspond to ages of up to 1,000,000 yr, need not be reliable due to these problems, even though they seem to agree with the paleomagnetic date.

STABLE OXYGEN AND CARBON ISOTOPE DATA

The stable oxygen and carbon isotope compositions were determined from samples taken only 1mm apart in the top 27cm (Fig 3). Hence, the time resolution should be better than one century and short-term climatic changes such as the transition between glacial and interglacial periods should be recognizable if they are inherent in the $\delta^{13}C$ and $\delta^{18}O$ values. Unfortunately, kinetic isotope fractionation, which may occur during deposition, often masks the paleoclimatic information (Fanditis & Ehhalt, 1970). In addition, the effects of diagenetic processes, such as recrystalliza-

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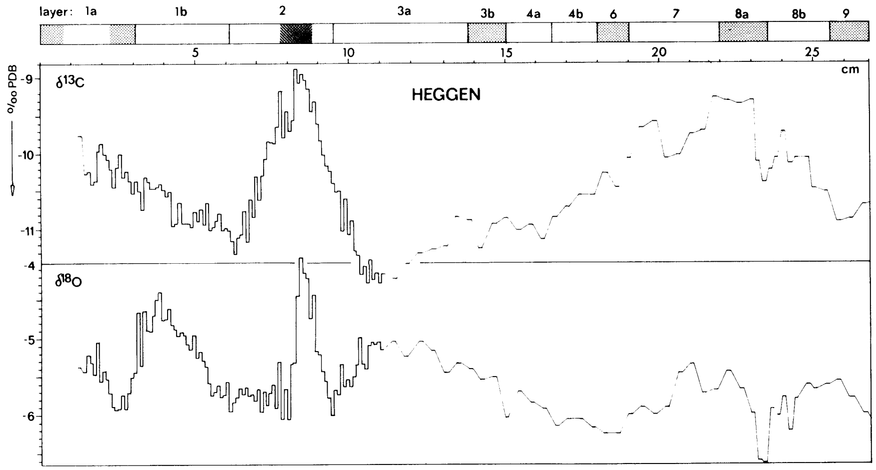

Fig 3. $\delta^{18}O$ and $\delta^{13}C$ records from the Heggen cave

tion or isotopic exchange, also make deciphering difficult. However, the surprising finding by Siegenthaler *et al* (1984) that four $\delta^{18}O$ records of different Swiss lacustrine sediments are similar, though not yet interpreted as climatic records, and are comparable to the Greenland ice record, made analogous studies of long-term growth of flowstones promising.

The $\delta^{13}C$ and $\delta^{18}O$ records from the Heggen cave are shown in Figure 3. Corresponding records from a Holocene stalagmite taken in the Mieru cave in Czechoslovakia (Geyh, 1970) look similar, although there are problems in the calibration of the time scales. Further attempts to compare stable isotope records from other Holocene stalagmites from the Aven d'Orgnac (Labeyrie *et al,* 1967), the St Kanzian cave in Yugoslavia, and the German caves, Maximilian and Kaminloch, have not been convincing.

Therefore, we only looked for peculiarities in the isotope records from the Heggen cave, paying special attention to Layers 3a and 3b as well as Layers 5/6 and 7, where the Pleistocene/Holocene or former glacial/interglacial transitions were expected. But nothing was found. The pronounced peak that occurs in both isotopic records is within the very dirty brown Layer 2, which might have been deposited during the Atlantic stage. The initial interpretation that the brown layers were formed from the debris in meltwater at the beginning of interglacial periods was, therefore, abandoned.

We now assume that during periods with a hot wet climate such as the Atlantic stage or Stage 5e in the isotope deep-sea record, the flowstone was recrystallized and the growing crystals pushed the impurities towards the surface. The remaining white calcite in the deeper part was formed before this process during less warm but still interglacial times.

There are also good indications that growth did not occur along this flowstone profile during interstadial periods. According to Geyh and Franke (1970), the growth rate of flowstone was one order of magnitude less during such periods than during interglacial periods. In our case, it would be only 0.7mm/1000 a, which might be on the order of the corrosion rate during glacial periods, which becomes apparent from the earlier, uneven surfaces.

If the flowstone grew ca 7cm during each of the ca 10 interglacial periods since the beginning of the Bruhnes epoch, the paleomagnetic reversal was correctly interpreted.

CONCLUSIONS

A geochronologic study of a million-year flowstone record is consistent with the assumption that it was formed almost exclusively during interglacial periods. Due to the very low growth rate of only several mm/1000 a, diagenetic processes, such as recrystallization in the range of centimeters, changed the isotopic composition within flowstone. Therefore,

- the boundaries of the transitions from glacial to interglacial periods cannot be exactly determined, neither by geochronologic data, such as ^{14}C, U/Th, or ESR, nor by sedimentologic analysis;
- paleoclimatic information from stable isotope dates may be masked by kinetic isotope fractionation during the deposition, as well as post-depositional changes in the isotopic composition resulting from isotopic exchange, precipitation of carbonates in fissures, or recrystallization.

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