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Deuterium isotope composition of palaeoinfiltration waters trapped in speleothems

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Final Report to the Research Contract No. 3660/RB

ABSTRACT.

Analytical and methodological aspects of combined isotope investigations of carbonate cave deposits are thoroughly discussed in the report. Weight is put on isotope analyses of fluid inclusions (D and ^{18}O content) extracted from speleothems of known age. Dating was done by the $^{230}Th/^{234}U$ ratio method . Isotopic analyses of speleothems originating from European caves allowed some important conclusions to be formulated regarding past climatic and environmental conditions prevailing over the European continent during the last 300,000 yrs: a) δD values of fluid inclusions suggest a remarkable constancy of the heavy-isotope content of European palaeoinfiltration waters recharged during interglacial periods, b) a climate-induced, long-term changes in isotopic composition of precipitation and surface air temperature over Europe can be characterized by the deuterium gradient of ca. 1.4 ‰/°C, c) an apparent constancy of the continental gradient in deuterium content of European palaeoinfiltration waters as judged from the fluid inclusion data suggests that atmospheric circulation over Europe did not undergo substantial changes for at least 300,000 years.

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F I N A L R E P O R T

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I. SCIENTIFIC BACKGROUND OF THE PROJECT.

Environmental isotope techniques are of increasing importance to palaeoclimatological research. The reconstruction of palaeoenvironments with the aid of isotope methods is based on isotopic composition of various materials as glacier ice, deep sea sediments, lacustrine carbonates, ancient plant remains, old groundwaters, etc. Two basic requirements should be fulfilled to make such reconstruction reliable:

a/ defined relationship between isotopic composition of this material and key climatic parameters (temperature, relative humidity, etc.) .

b/ ability of dating of the analysed material.

Carbonate cave deposits, known as speleothems, have been longely recognized as important source of information about past climatic fluctuations over continental areas. During the process of deposition of speleothems small amounts of the vadose seepage water being in fact a meteoric water infiltrating into the cave, are trapped within the deposited calcite forming the so-called fluid inclusions. Since growth episodes of speleothems can span very long time periods, covering in some cases major portion of Pleistocene, the water trapped within crystalline structure of speleothems is of potential importance to isotope hydrology as samples of palaeo-infiltration water in areas where speleothems have been deposited. Moreover, deuterium isotope analysis of fluid inclusions combined with ^{18}O content of speleothem calcite allows a reasonable assessment of the cave temperature during formation of the analysed speleothem layer. This makes possible a resonable estimate of the δD/temperature gradient for climate-induced long-term fluctuations of isotopic composition of precipitation and temperature at the given site.

II. MAIN GOALS OF THE PROJECT.

The following goals have been formulated when starting the work partially supported by the IAEA Research Contract 3660/RB.

1. Developing of the suitable dating technique for the speleothem calcite.
2. Establishing the procedure for quantitative recovery of fluid inclusions from the speleothem calcite without significant isotope fractionation effects.
3. A reconnaissance isotope analyses of speleothem samples.

III. REALIZATION OF THE PROJECT.

Dating of speleothems

As a basic technique for dating speleothems we developed in our lab the Th-230/U-234 ratio method. Details of the sample preparation and measurement procedures are given elsewhere [1,2]. This method is now in a routine use in our laboratory. Also the Electron Spin

Resonance (ESR) and the thermoluminescence (TL) methods were applied by us.

Extraction of fluid inclusions

In order to recover quantitatively the inclusion water from the analysed speleothem samples a special vacuum extraction system was developed and tested [3]. The reproducibility of δD values of the extracted fluid inclusions is about $\pm$ 2 ‰ . Numerous experiments showed that practically all water is removed from the host calcite, without visible fractionation effects.

δD and $\delta^{18}O$ analysis of the inclusion waters

The mass of the water extracted from speleothem samples varied between 8 and 100 mg. Since both D and O-18 content should be measured, a special sample preparation technique was necessary especially for O-18 analysis. For the O-18 determinations we applied an improved version of the CO_2-equilibration technique. Advantages and limitations of this technique are thoroughly discussed elsewhere [4]. Deuterium content of fluid inclusions was determined on a routine way using uranium method for hydrogen production. Proposed preparation scheme for D and O-18 analysis of fluid inclusion waters assures isolation of the sample from the atmosphere during the whole analysical run thus minimizing eventual evaporational losses and/or isotope exchange due to contact with atmospheric moisture.

IV. SUMMARY OF THE RESULTS.

In frame of the project altogether 40 speleothem samples originating from three different regions (Tatra Mts - southern and northern part, Krakow-Wielun Upland, Sauerland - Federal Republic of Germany) have been analysed. The following types of isotope analyses have been carried out on each sample:

a/ dating of the speleothem calcite (Th-230/U-234 ratio method, TL and ESR methods) ,
b/ deuterium and O-18 content of fluid inclusions,
c/ O-18 and C-13 content of speleothem calcite.

The results of isotope analyses of the investigated speleothem samples are thoroughly discussed in the attached publications. Here only short summary of the results will be given.

1. O-18 analyses of the inclusion waters confirmed earlier suspicions that primary O-18 content of fluid inclusions is modified by postdepositional isotope exchange with the host calcite. Detailed considerations of this process revealed that even under room temperatures it is fast enough to follow changes in the cave temperature induced by major climatic shifts. Consequently, the O-18 content of fluid inclusions is useless for further palaeoclimatic considerations.

2. Contrary to $\delta^{18}O$ value, deuterium content of fluid inclusions is preserved in speleothems since the time of their deposition. Owing to well defined relationship between isotopic composition of vadose seepage waters and local precipitation which in turn is controlled by climatic variables (mainly temperature), deuterium content of fluid inclusions extracted from speleothems of different ages will yield valuable information on past climates [5].

3. Deuterium content of fluid inclusions analysed sofar suggests a remarkable isotopic similarity of European palaeoinfiltration waters recharged during interglacial periods when compared to those presently formed in the study area. This evidence strongly supports ideas that interglacial climates in Europe were similar to those prevailing during Holocene. It is expected that reconstruction of deuterium isotopic composition of palaeoinfiltration waters can be extended even to tertiary climates, provided that suitable speleothem material become available.

4. Since cave are characteristic for their widespread occurence, it should be possible to reconstruct not only temporal but also spatial variability of deuterium content in palaeoinfiltration waters. Comparison of fluid inclusion data obtained for Polish speleothems with those originating from Federal Republic of Germany suggests an apparent constancy of the isotope continental gradient in European palaeoinfiltration waters during the last 300,000 years. Moreover, its similarity to the present-day gradient provides a new argument in favour of hypothesis that atmospheric circulation over Europe did not undergo substantial changes during the above mentioned period.

5. The isotope data for both the fluid inclusions and the host calcite provide a unique possibility to assess the δD/temperature gradient for climate-induced long-term fluctuations of isotopic composition of precipitation characteristic for the site of speleothem formation. This type of the isotope/temperature gradient seems to be the most relevant as far as palaeoclimatic applications of stable isotopes are considered. The mean value of this gradient as obtained from the analysed fluid inclusion data is equal ca. 1.4 ‰/°C.

V. CONCLUSIONS.

There is no doubt that speleothems represent one of most attractive sources of information on past climatic and environmental changes on continental regions and many oceanic islands. Especially isotope studies of speleothems were proved to provide a key data in this matter, very difficult to obtain in other ways.
The results obtained sofar in isotope studies of European speleothems look very promising and further work in this field would be highly desirable. Eventual further investigations should be concentrated in two areas:

a/ extention of the δD record in fluid inclusions back in time beyond the present age limit of the Th/U dating method. The ESR dating technique should be very helpful here.

b/ isotope studies of speleothems from other regions of Europe.

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ENCLOSURE.