

## Experimental test of the isotope equilibrium criterion in the case of limestone samples selected for paleotemperature measurements

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**Abstract.** Results of experiments carried out to test the isotope equilibrium criterion of reliable oxygen isotope paleothermometry, are presented, and some practical proposals are given. Approximate geological dating by the use of time-temperature correlation is also considered.

**Key words:** paleothermometry, oxygen isotope temperatures, temperature - age correlation.

### Introduction

In a previous paper (KECSKÉS - CORNIDES, 1992) we have considered the possibility of obtaining at least approximate age data in the case of limestone deposits taking into account the correlation found between the oxygen isotope ratio (usually given by the customary  $\delta^{18}\text{O}$  data) measured for a great number of marine limestone types and the age of these samples. There is a definite decrease of the  $^{18}\text{O}$  content with increasing age. Such a correlation is reasonable since the oxygen isotope ratio in question may often be used as a paleothermometer and, on the other hand, the temperature changes with time (age). These two relationships involve an indirect third one. This  $\delta^{18}\text{O}$  - age correlation in favourable cases may provide age data estimations, sequences in time, etc., which are quite useful if no reliable data are available.

For instance, if an investigation on the formation and geological history of limestone caves is to be carried out (in our case that of the stalactite caves in the region Liptov, Slovakia) it is of primary interest to obtain chronological information too. The most direct and therefore the conventional method of geological dating is based on the decay of radioactive isotopes. Unfortunately however, the concentration of these isotopes in the stalactites is quite often very low, and this results in high uncertainty of the age data.

A reasonable choice is offered by the fact that we need both the carbon and the oxygen isotopic ratio of the calcite in the samples taken from the stalactites. The  $^{13}\text{C}/^{12}\text{C}$  data usually present infor-

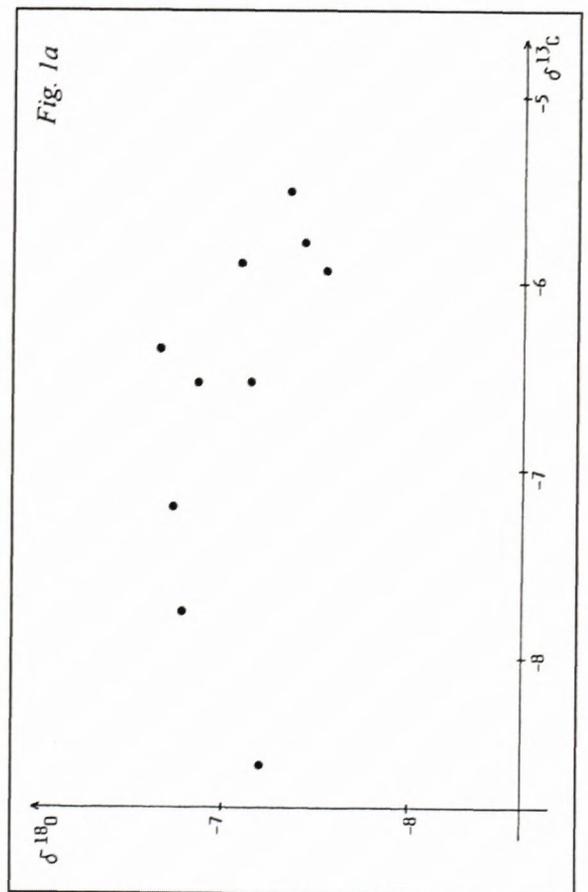
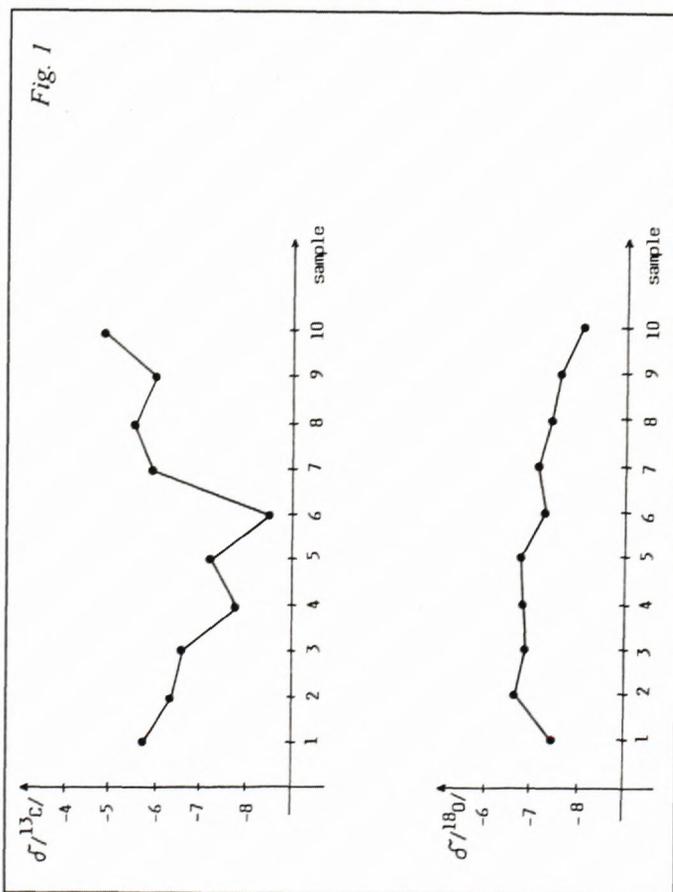
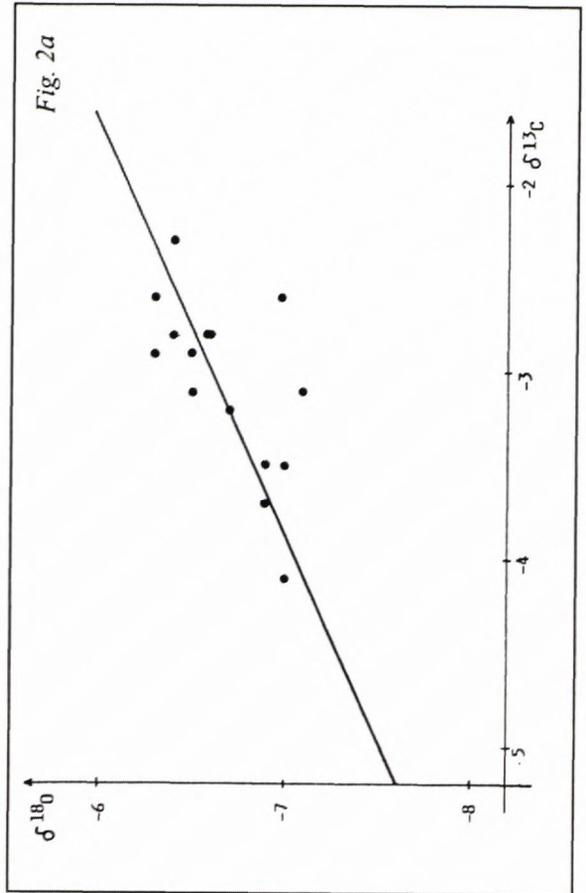
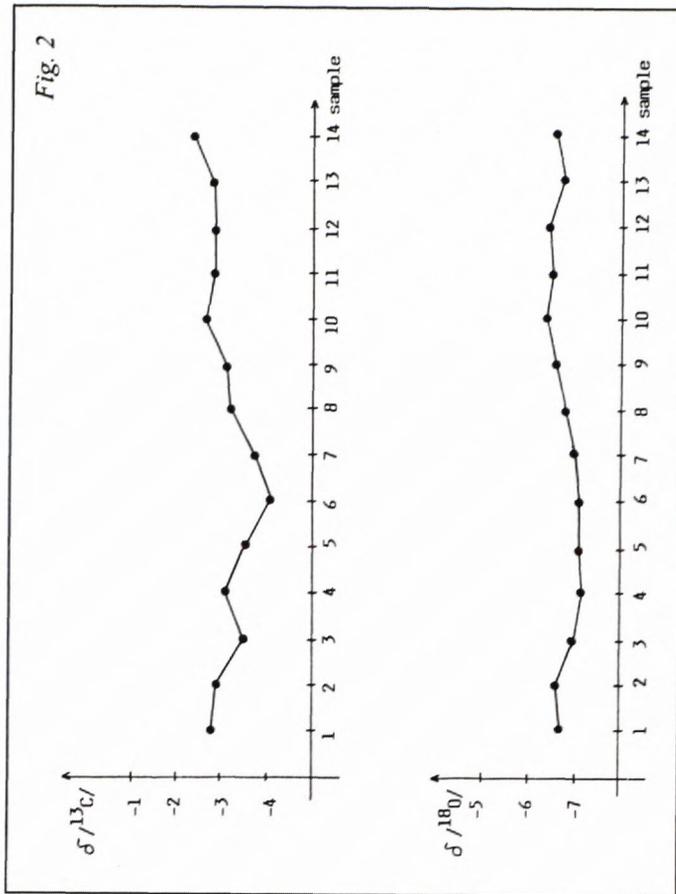
mation on the origin of the carbon (e.g. organic, metamorphic, magmatic) while  $^{18}\text{O}/^{16}\text{O}$  data provide the most sensitive and accurate paleoclimatic indicator, if properly used. Accordingly, oxygen isotope data will be at our disposal anyhow, and may be used also to try to figure out the chronology of the formation of caves to be investigated.

Thus, we have two reasons to use properly the oxygen isotope method of geochemistry. The measurement of the  $^{18}\text{O}/^{16}\text{O}$  ratio does not pose any problem in view of the present-day high performance mass spectrometers.

The basic problem is presented by the recognition that a strict condition limits the use of the stalactites, calcite material for paleotemperature measurement: the calcite must had to be deposited in isotopic equilibrium with the water of its solution, i.e. with the ground-water that had been seeping into the cave from above. Obviously, it is a crucial requirement to possess a reliable and sufficiently sensitive method to apply this "equilibrium fractionated deposition" criterion.

### Previous theoretical work

More than 20 years ago a paper was published by (HENDY, 1971) in which the isotope geochemistry of speleothems (a common term for both stalactites and stalagmites) is dealt with excellently. Taking into account all processes which lead to the precipitation of calcium carbonate to form speleothems, a detailed theoretical treatment is given to the isotope fractionation of the general process, in the case of both carbon and oxygen. As an important result the above criterion was formulated and also the principle of (the method of) its application was given: "Where the calcite has been deposited on a speleothem in isotopic equilibrium with the ground water, a variation in the  $\delta^{18}\text{O}$  of the calcite would only occur if there had been a variation in climate, and thus these speleothems may be used as paleoclimatic indicators. Speleothems which exhibit a straight-line relationship between variations in  $\delta^{18}\text{O}$  and variations in  $\delta^{13}\text{C}$  should be regarded with suspicion



since it is likely that this was caused by kinetic isotopic fractionations and it is thus likely that the calcite was not in  $^{18}\text{O}$  equilibrium with the water from which it was precipitated."

### Experimental

Our present work was intended to carry out experimental test of the criterion proposed by Hendy to obtain information on its practical application, including reliability and sensitivity.

Three sets of calcite samples were chosen for this investigation representing three different kinds of localities, much dissimilar environmental conditions and, therefore, quite different possibilities for isotopic equilibrium:

No.1.set /10 samples/: a remote and deep-seated part of the famous stalactite cave of Demänova/Liptov, Slovakia/.

No. 2. set /14 samples/: a part of a small limestone cave near to the entrance (Liptov, Slovakia).

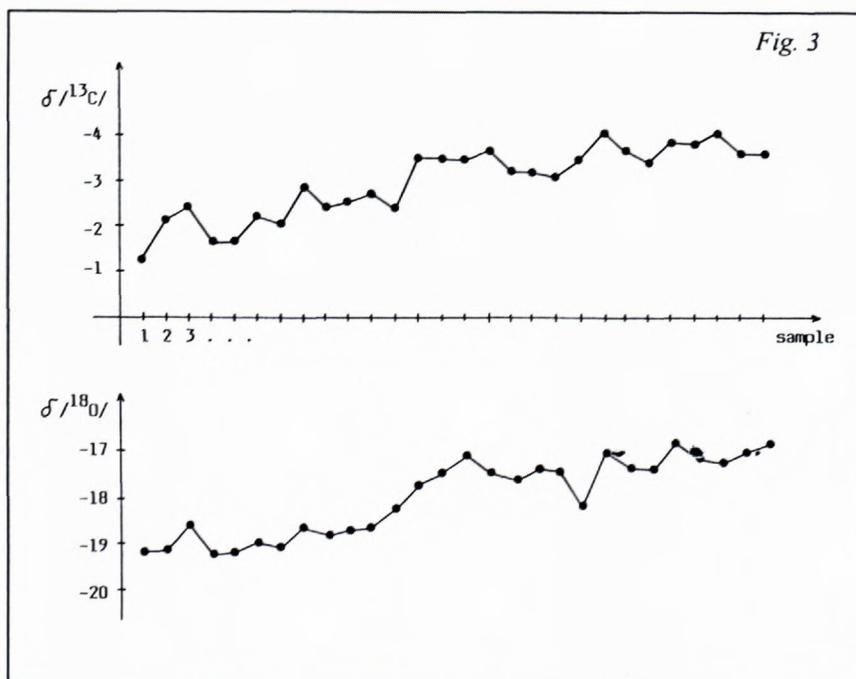
No. 3. set (28 samples): open-air limestone sediment, deposited from the water of a brook containing dissolved calcium carbonate. The individual samples of these sets provide time-sequences of calcite specimens (one for each set) offering the possibility of studying the relationship between the variations of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , respectively, under different conditions of the three localities. The calcite samples have been obtained from the stalactite specimens by boring out material along the symmetry axis i. e. in the direction of growing, at 0,5 cm distances. In the case of the open-air sediments the

samples were collected also at equal distances in the direction of the flow of the water from which the precipitation occurred. The isotope ratio measurements have been carried out (after applying the usual sample chemistry with phosphoric acid saturated to 100 per cent) using magnetic sector type isotope mass spectrometers with double collector system for gaseous samples, within the framework of interlaboratory cooperations (see acknowledgements). All mass spectrometers used have been manufactured by the same Finnigan MAT (Bremen) company and all are members of the same family of isotope mass spectrometers differing only in the degree of reproducibility, all being better than 0.1 % which is satisfactory for the investigation of correlation. The results related to the PDB standard are presented in Fig.1. to Fig.3.

### Discussion and Conclusions

As suggested by Fig. 1., no straight-line relationship (correlation) may exist between the oxygen and carbon isotope data in the case of the No. 1. set of samples. On the other hand, for the samples of the sets No.2. and No.3. such correlation can be predicted. These relationships can even be better visualized by the  $\delta^{13}\text{C} - \delta^{18}\text{O}$  diagrams shown in Fig.1a. to Fig.3a.

Our findings can be presented also in a more quantitative way by the use of statistical mathematics. We have calculated the correlation coefficient  $\rho$  ( $r$ ) for the relationship of the oxygen and carbon isotope data in the case of all three sets of samples.



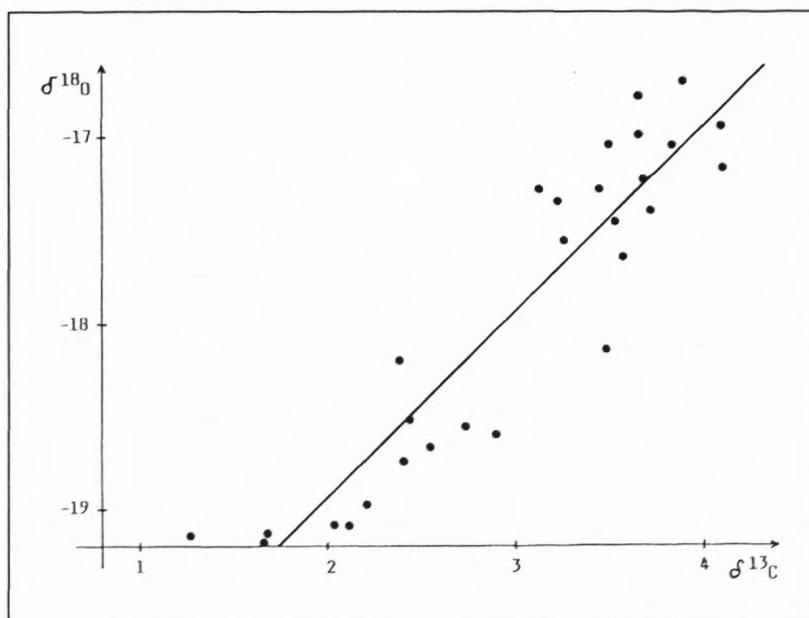


Fig. 3b

For the No.1. set  $\rho = -0,593$  was obtained, i.e. a rather low absolute value. For this reason no linear relationship may exist in this case and therefore - according to the isotopic equilibrium criterion - the samples of the No.1. set can be used for paleotemperature measurements, as we had hoped.

On the other hand, in the case of the sets No.2. and No.3. the rather high  $\rho = 0,79$  value, and the very high  $\rho = 0,925$  value have been obtained, respectively, which indicate strong linear correlation. This is demonstrated by the two straight lines drawn in Fig. 2a. and Fig. 3a., the position of which was calculated using the least squares method. Accordingly, the samples of the No.2. and No.3. sets are unsuitable for paleothermometry, as it was expected.

As conclusions we may point out that:

a/ The isotope equilibrium criterion as proposed by Hendy is a useful tool to obtain reasonable reliability of the oxygen isotope paleothermometry.

b/ For testing experiments, the measurement of a greater number of samples is to be used: 25-30, or more.

c/ An absolute value of the correlation coefficient less than 0,4 may guarantee an acceptable reliability of the oxygen isotope temperature data.

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