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Noble gas measurements from tiny water amounts: fluid inclusions in carbonates of speleothemes and coral skeletons

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Based on the concentrations of dissolved noble gases in fluid inclusions in speleothems and corals, noble gas temperatures (NGT) might be derived, that would be important climate information [1]. In the case of terrestrial carbonates, it means that the temperature dependency of noble gases in the evolving fluid inclusions is suitable to determine the prevailing temperature. This recognition provides new opportunities for the research of paleoclimate. Additionally, the dissolved noble gases in the fluid inclusions represented in corals could be used to study past sea surface temperatures that are one of the most essential parameter of climate reconstructions. To measure dissolved noble gases in fluid inclusions of a few micro-litres, a noble gas mass spectrometer equipped with an ultra high vacuum preparation line is the most suitable way.

The preparation of the carbonate samples is performed in a sample preparation system connected to a static mode VG 5400 noble gas mass spectrometer. As a first step of the sample preparation, one piece of a sample is put into a crusher of the preparation line and then evacuated and heated at night. The crushing of dripstone and coral samples is carried out in a stainless steel pipe with a ferro-magnetic ball at 150 ºC temperature, in such a way that the ball is kept on elevating and falling down onto the carbonate sample one hundred times. The aim of the heating is to avoid the water released from the fluid inclusions not to be adsorbed on the surface of the freshly broken carbonate [2]. The water released from the fluid inclusions is frozen into a cold finger, being held at temperature of -70 ºC for 15 minutes. In this case, the collection efficiency is better than 99.7 %. Then the cold finger is warmed to 27 ºC, and the pressure of the water vapour expanded to the volume of the cold finger is determined by a pressure gauge, which accuracy is better than 0.2 % in the pressure range of 10-2 mbar to 11 mbar. The water vapour pressure range has been calibrated by measuring ten well known water aliquots between 0.45 mg and 3.14 mg sealed in glass capillaries. With this method, the quantity of the water can be determined better than 1% uncertainty. After the dissolved noble gases has been released from the fluid inclusions, they are collected and separated from each other by a cryo system which consists of a stainless steel empty trap and a trap filled with charcoal. The argon, krypton, xenon fraction and the other chemically active gases (N2, O2, CO2, etc.) are trapped in the stainless steel trap at 25 K, while the isotopes of helium and neon in the charcoal trap held at 10 K. So far, the abundance of helium is not measured, because helium does not play a role in the NGT determination due to radiogenic helium component. The helium is pumped away.

The neon is released from the stainless steel trap at temperature of 90 K and admitted to the noble gas mass spectrometer. The ion source is tuned for the best sensitivity for neon. The neon isotopes are detected by an electron multiplier in ion counting mode. The argon, krypton and xenon isotopes are measured simultaneously. The gases are released from the stainless steel trap at 150 K, and introduced into a getter trap in order to be purified from the other non-inert gases. Then the pure argon, krypton, xenon fraction is admitted to the mass spectrometer. The isotopes of argon are detected by a Faraday cup, while krypton and xenon isotopes are detected by an electron multiplier. After every single mass spectrometric measurement fast calibration are executed. The calibration of the mass spectrometric measurement is performed by means of well known air aliquots taken from an air reservoir in which the pressure is 2.0052 Pa.

The results of the calibration measurements show that the reproducibility is about 2% for all noble gas isotopes measured. This error in noble gas concentrations results in an uncertainty of about 1 ºC or lower in the determination of NGT, if the amount of the excess air is smaller than 10 V/V %. To check the overall precision of our measurements, standard water samples of a few micro-litres have been prepared. Air equilibrated water has been closed in copper capillaries. The measurements reflected the same precision obtained in the measurements of air calibrations.

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[2] Dennis P.F., Rowe P.J., Atkinson T.C., 2001. Geochimica et Cosmochimica Acta 65, 871-884.