the autosampler while the second needle transfers the evolved gas from a neighboring vial into the GasBench. This procedure ensures identical reaction times. Following water removal using Nafion traps, CO_2 is separated from other components of the gas sample using a gas chromatographic column (heated to 70.0°C) and the peak of this CO_2 is then sent through an open split into the MS.

Measurements are performed on a Delta^{plus}XL MS. Each sample run starts out with a peak centering, followed by three rectangular-shaped mass peaks of CO_2 reference gas, after which nine successive sample peaks are produced by delivering nine sequential aliquots of pure CO_2 into the ion source. The internal precision (1 sigma) is typically 0.03-0.06‰ and 0.04-0.08‰ for raw $\delta^{13}C$ and $\delta^{18}O$, respectively. We use an in-house calcite standard (sieved Carrara marble, calibrated against NBS 18, 19, CO-1 and CO-8) to calibrate the raw results versus the VPDB scale. The external precision calculated over 12 standards per batch is typically 0.05-0.06‰ for $\delta^{13}C$ and 0.06-0.08‰ for $\delta^{18}O$. The standard deviation for the QA sample (Laas marble) over a 14 month measurement period is 0.065‰ and 0.075‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively, which compares favorably to other labs (e.g., Revesz et al., *U.S. Geol. Survey Open-File Report 01-257, 2001*; Werner & Brand, *Rapid Comm. Mass Spectrom., 15, 2001*).

Rain-gauge with integrated isotope-sampling device

H. Stadler

Joanneum Research, Institute of Hydrogeology and Geothermics, Graz, Austria

This precipitation station is designed to measure the rainfall and to offer the possibility to take samples for isotopic analyses of the total discharge during one month.

Precipitation measurement: Digital tipping bucket rain-gauge with a time resolution from one minute up to some hours (free of scaling) and a quantity resolution (depending on the type of bucket) from 0.1 or 0.2 mm rainfall.

Sampling application: For isotopic analyses it is necessary, that no part of the precipitation can evaporate. Therefore in this application the containers where the precipitation are stored, can be opened and closed. This procedure is working automatically. When the rainfall starts (=the moment of the first tipping), the container is opened. After the rainfall it is closed again. The time of delay can be chosen individually (for instance 1 to 10 minutes).

To get correct samples of one month, a second valve is changing the flow path between the two containers exactly at the beginning of the month.

The schematic construction of the isotope sampling device is shown in Fig. 1.

COLLECTING FUNNEL

TIPPING BUCKET

M VALVE OPEN/CLOSE
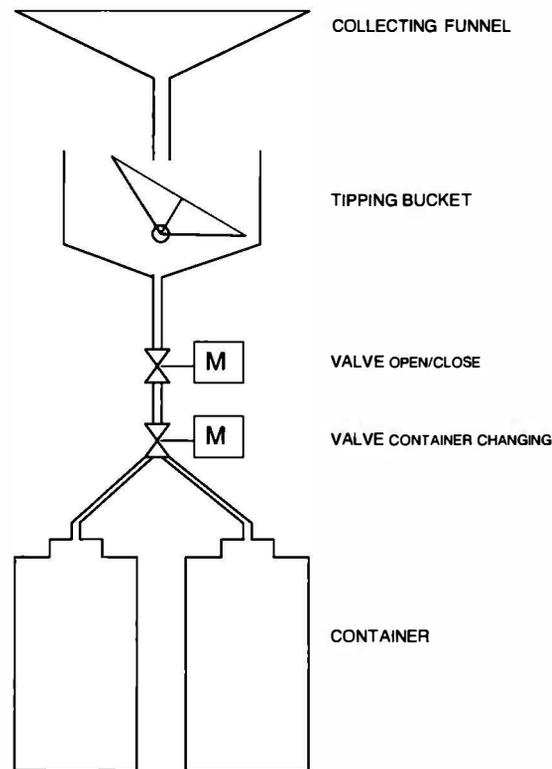
M VALVE CONTAINER CHANGING

CONTAINER

Fig. 1: Scheme of the automatic isotope-sampling device.
Both valves are controlled by the data-logger. Apart from precipitation also other parameter like temperature, wind speed, radiation, and so on can be stored.

EXISTING COLLECTING FUNNEL

NEW TIPPING BUCKET

DATALOGGER

ELECTRICAL HEATING

THERMOSTAT

VALVE FOR OPENING AND CLOSING THE CAN

VALVE FOR CHANGE OF THE CONTAINER (MONTHLY)

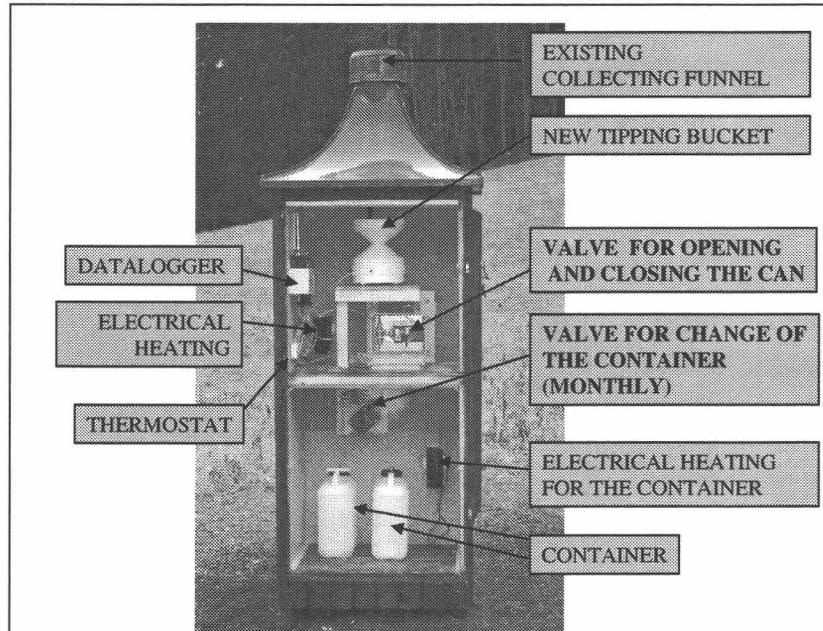ELECTRICAL HEATING FOR THE CONTAINER

CONTAINER

Fig. 2: Automatic precipitation station with integrated isotope-sampling device.
The picture shows a station of the Zentralwasserversorgung Hochschwab Süd, rebuilt with the digital equipment and the isotope sampling device.

The whole application can be mounted in existing measuring stations, without changing the existing collecting funnel (as shown in Fig.2). This is important for the continuity of the measurement at an existing station.

To avoid large changes of temperature of the sampled water, the containers can be isolated. The station must be heated in such a way, that the sample is not freezing. A simple funnel heating is not enough. The heating can be done with gas or electricity. Electrical heatings can be regulated by a thermostat. In stage of development are funnel-heatings with Peltier-elements. This devices are also able to cool the collecting funnel during hot periods.

The system (without the heating) can be supplied with solar panels and supplemented with remote data transfer systems like LEO-satellites, GSM or telephone.

The ^{13}C/^{12}C fractionation Upon the Setting of Calcium Carbonate Mortars

E. Usdowski

Geowissenschaftliches Zentrum der Universität Göttingen
D-37077 Göttingen, Germany

A number of sciences has become more and more concerned with the constituents of historical mortars. For example, in archaeology the objective is to deduce from the mineralogical and chemical compositions the provenance of material or even former recipes and methods for preparation, and environmental sciences are specially concerned with the carbon isotopes of the calcium carbonate of lime mortars in order to derive a former composition of atmospheric carbon dioxide. Under such auspices it has been shown that the sulfur isotopes of gypsum mortars may be used in order to trace the origin of the raw material. However, lime mortars represent a much more complicated case, because their calcium carbonate displays a rather wide range of compositions from $\delta^{13}C \approx -25$ to -7 $^o/_{oo}$ (PDB) and from $\delta^{18}O \approx 8$ to 24 $^o/_{oo}$ (SMOW). Obviously, this range reflects various processes of isotopic fractionation which occurred during the history of an individual cement. But it is not clear which of the data may represent a primary composition.

In order to establish this composition experimental brickwork has been set up. Surprisingly, the measurements show that, unlike to the sulfur isotopes of gypsum mortar, the calcite of lime mortar does not have a unique carbon isotope composition. The $\delta^{13}C$ values change systematically from -11 $^o/_{oo}$ at the outside of the brickwork to -2 $^o/_{oo}$ (PDB) within the interior at a very good correlation to the oxygen isotopes. This zoning along a mortar layer is caused by a kinetic fractionation factor $\alpha_{CaCO_3-CO_{2(g)}} = 0.9960$ which is given by the absorption of atmospheric carbon dioxide into a strong alkaline slurry of portlandite, sand and water and its subsequent reaction to calcite within a liquid boundary layer surrounding the $Ca(OH)_2$ particles. Thus, the diffusion and the reaction of carbon dioxide leads to an enrichment of ^{13}C over ^{12}C at the gas-side of a reaction front so that the calcite becomes continuously "heavier" from the exterior to the interior along a mortar layer. The overall process may be described by a fractionation according to zone melting. The variation of the oxygen isotopes follows the same principle. However, a reliable fractionation factor is difficult to assess.