

as measured during the calcite runs. Overall external precision quoted at the 1-sigma uncertainty level typically is 0.1‰ for $\delta^{13}\text{C}$.

In alpine karst aquifers $\delta^{13}\text{C}_{\text{DIC}}$ depicts large variations that are seasonally controlled. In the Obir Caves underground study site (Carinthia) drip waters show a consistent pattern of low $\delta^{13}\text{C}_{\text{DIC}}$ values during the warm season. The midpoint of the transition from high and low values (change from winter to summer regime) occurs between mid April and June, depending on the location in the cave system. Conversely, the midpoint of the rising trend of $\delta^{13}\text{C}_{\text{DIC}}$ values at the end of the warm season occurs between early to mid November. The lowest values (during summer) are -12.7 to -11.2 ‰ (11 sites), whereas cold-season values typically reach up to -2.9 ‰. The low $\delta^{13}\text{C}_{\text{DIC}}$ values are consistent with a simple mass-balance calculation in which dissolved soil CO_2 (-24 ‰) and limestone host-rock ($+3$ ‰) contribute approximately 85% and 15% of carbon to the solution, respectively. This mixing proportion deviates significantly from the stoichiometric calcite dissolution equation but is typically observed in karst systems based on ^{14}C studies (e.g., Genty et al., *Radiocarbon*, 41, 1999). The tendency toward high $\delta^{13}\text{C}_{\text{DIC}}$ values during the cold season could be attributed to low soil bioproductivity and hence a higher proportion of ^{13}C -rich carbon in the aquifer. Comparison with other parameters, however, strongly implies that it is more likely to be a result of kinetic effects inside the cave environment and in particular due to seasonally changing underground air flow causing low pCO_2 values in winter which give rise to degassing of cave seepage waters, secondary calcite precipitation and enrichment of the residual vadose waters in ^{13}C .

Continuous-flow IRMS analysis of carbonates using the GasBench II

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Stable isotope (C, O) analysis of carbonate minerals (predominantly calcite) is a standard procedure in a wide range of geoscientific research fields, including paleoceanography and terrestrial paleoclimate studies. The classical method used to obtain C and O isotope ratios in calcite (McCrea, *J. Chem. Phys.*, 18, 1950) is labor intensive and requires large sample sizes (tens of milligrams) and each sample must be prepared by hand. Automatization has led to the development of online carbonate preparation lines hooked up to dual-inlet isotope ratio mass spectrometers (IRMS). The advent of continuous-flow techniques has significantly simplified and streamlined this technique.

A GasBench II linked to a Delta^{plus}XL mass spectrometer was installed at the Department of Geology and Paleontology of Innsbruck University in 2000 and since spring of 2001 this system has been extensively used to run a large amount of powdered carbonate samples (ca. 27.000 samples since January 2001), which are being prepared using a video-controlled micromilling device. Our system routinely handles sample sizes between approximately 100 and 450 μg that are directly loaded into 10 ml borosilicate exetainers and sealed using butyl rubber septa (Labco). 72 exetainers are placed into an aluminum tray kept at $72.0 \pm 0.1^\circ\text{C}$, including 12 standards and one quality assurance standard. During a first step the exetainers are automatically flushed with 6.0 He by penetrating the septa using a double needle. Afterwards, 5-7 drops of phosphoric acid (density 1.91) are deposited in each exetainer using

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, CO₂ is separated from other components of the gas sample using a gas chromatographic column (heated to 70.0°C) and the peak of this CO₂ 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 CO₂ reference gas, after which nine successive sample peaks are produced by delivering nine sequential aliquots of pure CO₂ into the ion source. The internal precision (1 sigma) is typically 0.03-0.06‰ and 0.04-0.08‰ for raw $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, 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 $\delta^{13}\text{C}$ and 0.06-0.08‰ for $\delta^{18}\text{O}$. The standard deviation for the QA sample (Laas marble) over a 14 month measurement period is 0.065‰ and 0.075‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, 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

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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.

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Artikel/Article: [Continuous-flow IRMS analysis of carbonates using the GasBench II 33-34](#)