

δD values of bird feathers are related to their geographic location during molting (feather growing). An isotopic study of Wilson's warblers shows that birds migrating to the most northern latitudes in summer, also migrate to the most southerly latitudes in winter, 'leapfrogging' a second group of Wilson's warblers that migrate far less. This kind of migration information was unknown before our isotope study. In another study, the δD values of the Aconcagua Mummy sacrificed in the high Andes were measured. H, C, N and S isotope ratios all varied as a function of seasonality. We were able to show that the mummy child had not lived at high altitudes for a significant period of time prior to his death.

We have coupled the continuous flow hydrogen method with a laser extraction system to extract single fluid inclusions for δD determinations. We find that primary and secondary fluid inclusions have distinctly different δD values. Primaries have mantle values; secondaries have a strong meteoric component. We have also started a program of analyzing the δD of atmospheric water vapor. Unlike typical meteoric water measurements, which can only be made when it rains, we can analyze vapors at any time, and our data are consistent with the actual air, not the water modified by condensation-evaporation processes.

Because hydrogen is a major constituent of water and organic matter, and to a lesser extent, rocks, its applications are extremely varied. The advances of rapid turnover time, small amounts of material for analysis, and the high spatial resolution when coupled to a laser, means that a tremendous number of new applications will be seen in the coming years.

The stable isotopic composition of DIC in karst groundwater: Methodology and applications

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The stable isotopic composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) is a useful parameter to trace the origin(s) of the bicarbonate ion, which is the dominant anion in shallow groundwater. In this setting, DIC has three main sources, soil carbon dioxide, dissolution of carbonate minerals, and atmospheric carbon dioxide exchanged through the air-water interface.

We use a gas evolution method that (a) avoids the use of toxic additives to prevent microbial activity, (b) requires only small sample volumes, and (c) works reliably and quickly even in difficult field conditions (e.g., caves). 10 ml sample vessels are preloaded with a few droplets of phosphoric acid, capped, and the head space is flushed with He. In the field, the sample is injected into the exetainer using a needle syringe. The amount of sample depends on the carbonate alkalinity and varies from fractions of a milliliter up to 2 ml. The CO_2 in the headspace of the exetainer is analyzed within a few days using a Delta^{plus}XL isotope ratio mass spectrometer operating in continuous-flow mode (GasBench II). We found no significant (i.e., > 0.1‰) C isotope shift during a few days of sample transport and storage (cf. Nelson, *Rapid Comm. Mass Spectrom.*, 14, 2000; Tu et al., *Rapid Comm. Mass Spectrom.*, 15, 2001).

Because there are no durable DIC standards available, we use the following procedure to calibrate the raw delta values against VPDB: DIC samples are run intermittently with calcite samples (DIC is measured during the working day, calcite runs over night). We use the calcite standard $\delta^{13}C$ values of the runs before and after a DIC measurement to correct and calibrate the DIC values. A linearity correction is performed using the slope $\delta^{13}C$ vs. intensity of mass 44

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