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RCM

Letter to the Editor

To the Editor-in-Chief
Sir,

High-precision oxygen and carbon isotope analysis of very small (10–30 μg) amounts of carbonates using continuous flow isotope ratio mass spectrometry

One of the major applications of stable isotope geochemistry is the estimation of palaeoenvironmental parameters from $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios (commonly expressed as $\delta^{18}O$ and $\delta^{13}C$ versus VPDB) of calcareous hard parts of fossil marine organisms. One of these parameters is ocean temperature. Past variations are compared to instrumental records in order to understand present day and, possibly, future climatic change. Isotopic analysis of carbonates greatly benefited from the development of continuous flow isotope ratio mass spectrometry (CF-IRMS, e.g., Matthews and Hayes[1] and Merritt and Hayes[2]). For the purpose of CF-IRMS, new automatic carbonate preparation techniques such as the Gas Bench II (Thermoquest) were designed that helped to significantly improve the daily sample throughput, with sample size as small as 50 μg.

An effective sampling and correction strategy for isotopic analysis of carbonates using the Gas Bench II has recently been described by Spoetl and Vennemann.[3] Following their procedure, external precision (1σ) is better than 0.07‰ for $\delta^{13}C$ and 0.08‰ for $\delta^{18}O$ for sample sizes >50 μg. For lower amounts (20–50 μg), external precision drops drastically with decreasing sample size (T. Vennemann, personal communication) and averages to 0.12‰ for $\delta^{13}C$ and 0.16‰ for $\delta^{18}O$, respectively. Considering that a temperature difference of 1°C corresponds to a $\delta^{18}O$ variation of approximately 0.2‰, only temperature variations >1°C can be reliably identified utilizing sample amounts <50 μg. However, the decrease in precision for sample sizes <50 μg is caused by the fact that the major amount of analyte CO_2 is discarded during isotopic analysis. In what follows, we describe a new cryofocus setup of the Gas Bench II that enables isotopic analyses of carbonate quantities as small as 10–30 μg with external precisions indistinguishable from those of the ''routine'' setup of Spoetl and Vennemann[3] with sample sizes >50 μg.

Our analytical setup equals that described by Spoetl and Vennemann[3] with the following major modifications: (1) we use a Thermoquest MAT 253 dynamic range mass spectrometer and (2) the sample loop at the 8-way Valco valve is replaced by a cryofocusing unit, that is commercially available from Thermoquest. It consists of a U-shaped 1/16″ stainless steel tube with Ni-wire inside (cryofocus) and a 2l Dewar for storage of liquid nitrogen. The tube is fixed to a pneumatically operated lifting unit and placed above the Dewar. The Isodat software supports vertical movement of the lifting unit such that the cryofocus can be

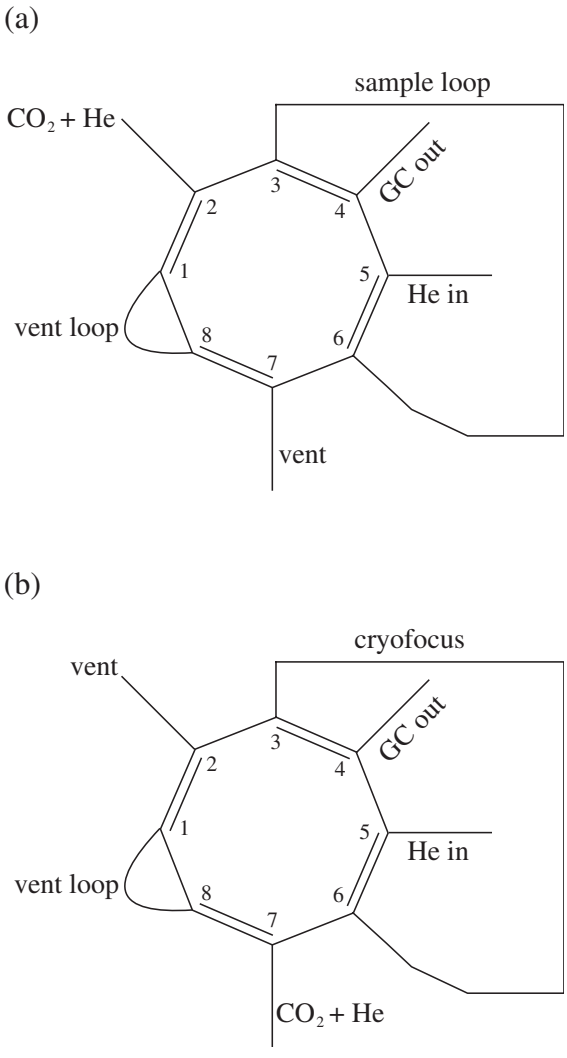

Figure 1. Configuration of the 8-port Valco valve of the Gas Bench II (a) for the ''routine'' setup according to Spoetl and Vennemann[3] and (b) for the cryofocus setup (this study). Note that (b) is distinct from (a) in that the sample loop is replaced by the cryofocus unit and ports 2 and 7 are exchanged against each other. Both (a) and (b) are schematically shown in the ''inject'' mode.