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Determination of clumped isotopes in carbonate using isotope ratio mass spectrometry: Toward a systematic evaluation of a sample extraction method using a static Porapak^{TM} Q absorbent trap

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ABSTRACT

In this study, we performed a detailed comparison of stable and clumped isotopic data for an extraction method passing CO_2 through a Porapak Q absorbent trap (PQT) driven by liquid nitrogen (LN method), an extraction method passing CO_2 through a PQT driven by liquid nitrogen and high vacuum pumping (LN + HV method) and an extraction method without a PQT (NAT method), to examine the effectiveness and reliability of these methods. Changes in raw Δ_{47} values along with collection times were used to constrain the optimum collection time (OCT) for each method. The OCT for the LN method shortened considerably when the PQT was warmer, i.e., from ~35 min to ~30 min when the PQT temperature changed from −15 °C to −12.5 °C. In contrast, the OCT for the LN + HV method displayed little change with the PQT temperature and was reduced to 25 min for both −15 °C and −25 °C. The contaminant removal efficiency of these methods was evaluated by Δ_{48} values, revealing that the LN method (with a −12.5 °C to −25 °C PQT) and the LN + HV method (at −25 °C) could effectively remove contaminants compared with the NAT method. Therefore, the LN + HV method (at −25.0 °C) may serve as a promising sample preparation method for routine measurement because it can save time without compromising sample cleaning efficiency. Nevertheless, the LN + HV method yielded Δ_{47} values 0.04–0.05‰ higher than the LN method at the same temperature, possibly because of different absorption–desorption states of the PQT in these methods. These findings provide useful clues for optimizing CO_2 extraction methods for clumped isotope analysis.

1. Introduction

Clumped isotopes are multiply substituted isotopologues (molecules containing two or more rare isotopes) and are a relatively new research direction in geochemistry. Recently, clumped isotope compositions of carbonate (expressed as Δ_{47}; quantifying the excess abundance of CO_2 with mass 47 ($^{13}C^{18}O^{16}O$) in carbonate) have been developed as a useful thermometer [1]. Clumped isotope thermometry has an advantage over conventional oxygen isotope thermometry in cases where the isotope composition of the water is unknown. Therefore, the clumped isotope thermometer enables a more precise reconstruction of paleotemperature than the oxygen isotope thermometer. This technique has been recently applied to determine the body temperatures of some extinct vertebrates and dinosaurs [2,3], to reconstruct changes in environmental temperatures during the geological past [4–6], to constrain diagenetic alteration [7] and to elucidate the uplift history of high mountains or plateaus [8].

Although clumped isotope thermometry has such broad applications, a large discrepancy still exists when comparing data from different laboratories. For example, the maximum difference in Δ_{47} values generated by various laboratories for the same carbonate substances in a recent inter-lab calibration reached up to 0.07‰ (Stefano Bernasconi, personal communication), corresponding to a temperature difference of approximately 15 °C or greater. The reasons for this large discrepancy may be manifold. Previous studies have shown that instrumental tuning parameters [9] and pressure imbalances between reference and sample CO_2 gases in dual-inlet mode [10] can affect the accuracy and precision of clumped isotope analysis. Other than effects from the mass spectrometer itself, the sample extraction method may be an important aspect to consider, especially when laboratories employ different processes for

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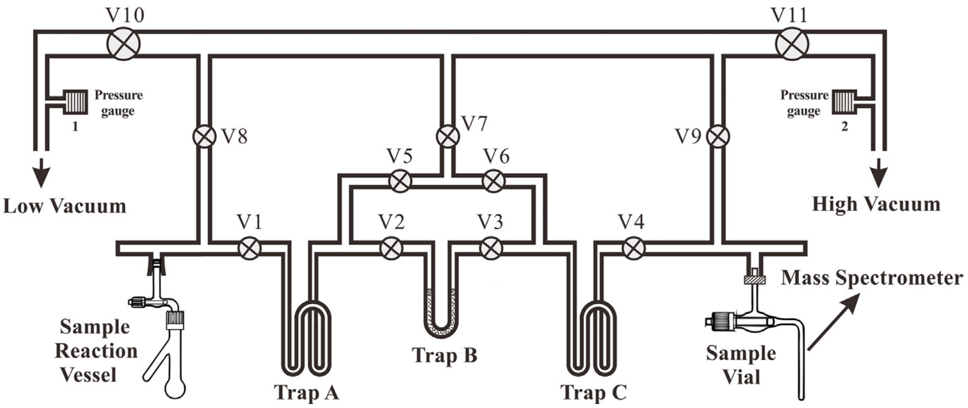

Fig. 1. Schematic map showing the collection and purification apparatus of the CO_2 produced from the phosphoric acid digestion of carbonate. Product CO_2 is cryogenically purified from water and other trace gases by passing through Trap A and Trap C, which are sequentially immersed in liquid nitrogen and a liquid nitrogen/acetone slurry. Trap B, the Porapak Q absorbent trap usually maintained at −15 °C (by immersion in a liquid nitrogen/ethylene glycol slurry), could be optionally used for the purification of hydrocarbons in this study. The CO_2 passes through Trap B if valves V2 and V3 are open and valves V5 and V6 are closed. Otherwise, the CO_2 will circumvent Trap B if valves V2, V3, and V7 are closed while valves V5 and V6 are open. Pressure gauge locations are marked as 1 and 2.

CO_2 extraction from carbonates. For example, Wacker et al. [11] studied reaction mechanisms of two different acid digestion techniques – a conventional sealed vessel method (at 25 °C) and a common acid bath method (at 90 °C), and a sample size effect on Δ_{47} values was observed for carbonates digested using the conventional sealed vessel method. To remove isobaric interferences from contaminant gases, i.e., hydrocarbons and halocarbons [12], CO_2 liberated from carbonate has been subsequently purified using two different methods: the CO_2 is entrained in a He stream flowing through a gas chromatography capillary column packed with a porous divinyl benzene polymer at −10 °C or −20 °C [1,13,14], or the CO_2 is passively passed through an absorbent trap filled with Porapak Q^{TM} (divinyl benzene polymer, 80–100 mesh) at −10 °C to −35 °C [7,15,16]. However, the extraction method using a Porapak Q absorbent trap has not yet been systematically evaluated, although it is routinely employed in Δ_{47} analysis in some laboratories.

In this study, we performed a series of contrasting experiments to examine the effectiveness of the Porapak Q absorbent trap (PQT) extraction method for CO_2 purification. The differences in measured Δ_{47} values for CO_2 extracted from pure carbonates were determined using two different methods: passing through the absorbent trap and circumventing the absorbent trap. This may provide useful future guidance to optimize sample extraction for clumped isotope analysis. To the best of our knowledge, no systematic research has been published on this issue.

2. Experimental

2.1. CO_2 extraction method

A Chinese national stable isotope standard (GBW04406) and three laboratory working standards (IVA, NB4 and P1) were analyzed for clumped isotopes. GBW04406 (calcite, supplied by the National Bureau of Standards of China) is a pure chemical reagent powder with certified $\delta^{13}C = -10.85‰$ (VPDB) and $\delta^{18}O = -12.40‰$ (VPDB). IVA (calcite, supplied by IVA Corporation, Germany) is a fine-grained chemical reagent with measured $\delta^{13}C = +2.21‰$ (VPDB) and $\delta^{18}O = -1.90‰$ (VPDB). NB4 (calcite, from Beijing Geological Museum, China) is coarse-grained white marble, which was crushed to a fine powder and homogenized using a mortar and pestle. P1 is a fine-powdered coral material, collected in Thailand. Our prior work indicated that these samples span a range of isotopic compositions and formation temperatures. We extracted CO_2 from carbonates by reaction with anhydrous phosphoric acid, generally following the method of Ghosh et al. [1]. Briefly, approximately 15 mg of sample was reacted with ∼103% phosphoric acid (density 1.90 g/ml) under vacuum at 25 °C for ∼16 h (overnight). The phosphoric acid was made by mixing an originally crystallized phosphoric acid (≥99%, Sigma–Aldrich) with phosphorus pentoxide powder (99%, Sigma–Aldrich). The CO_2 product was cryogenically purified by passing sequentially through different traps.

To examine the differences in measured Δ_{47} values for CO_2 purified using different extraction methods, we designed a glass extraction line with an optional pass through the Porapak Q absorbent trap (Fig. 1). The PQT used in this study was a glass U-tube trap densely packed with Porapak^{TM} Q (divinyl benzene polymer, 80–100 mesh) with packed material of 8 cm in length and ∼8 mm in diameter.

We adopted two different collection processes for purification extraction using the PQT: one with the CO_2 passing through the absorbent trap cryogenically drawn by liquid nitrogen (LN method), and the second with the CO_2 passing through the absorbent trap driven by liquid nitrogen and a high vacuum pump (LN + HV method). The LN method consists of the following procedures. (1) The CO_2 was first frozen in a U-shaped trap (Trap A) at the temperature of liquid nitrogen, and the trap was subsequently changed to a liquid nitrogen/acetone slurry trap at −80 °C to release the CO_2 while the water was still frozen. (2) The evolved CO_2 passed through the PQT (Trap B) immersed in a liquid nitrogen/ethylene glycol slurry (around −15 °C) and was then collected in another U-shaped trap (Trap C) at the temperature of liquid nitrogen with an optimal collection time determined during the study. (3) Once a given collection time was reached, the trap (Trap C) was subsequently changed to a liquid nitrogen/acetone slurry trap at −80 °C to freeze any trace amount of water, and the released CO_2 from Trap C was then collected in a small glass sample vessel using liquid nitrogen for clumped isotope determination. The LN + HV method generally follows the above LN method procedures except for the second step, which is described as below: the evolved CO_2 was drawn through the PQT (Trap B) immersed in a liquid nitrogen/ethylene glycol slurry (around −15 °C) with V2 and V3 simultaneously opened and collected in Trap C using liquid nitrogen. It was then continuously pumped on by a high vacuum pump downstream of Trap C through opening V4, V9 and V11. In contrast, the extraction method without purifying through a PQT (NAT method) only involved the removal of water from the CO_2 by two water traps (Trap A and Trap C) immersed in liquid nitrogen/acetone slurries (−80 °C). Prior to extraction of next sample, the PQT was heated