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Determination of clumped isotopes in carbonate using isotope ratio mass spectrometer: Effects of extraction potential and long-term stability

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ABSTRACT

In this study, we developed an instrument tuning method for analyzing clumped isotope on carbonates using isotope ratio mass spectrometer (IRMS). The ion source extraction potential is found governing accuracy and precision for CO_2 clumped isotope analysis, with 90% extraction as an optimum parameter. Under this condition, we obtained a relatively stable linearity of mass spectrometer, as shown by little variation in slopes (0.0075–0.0077) for three heated CO_2 gas lines (plot of Δ_{47} vs. δ_{47}) observed over a period of one year. By contrast, the intercepts of the heated gas lines displayed a larger variation, ranging from −0.79‰ to −0.89‰, which may be partially contributed by some artificial factor, e.g., variable cooling rates of heated CO_2 gases. Nevertheless, repeated measurements on NBS 19 demonstrate long-term reproducible Δ_{47} values, comparable with previously published results. The stable linearity of the IRMS results ensures that clumped isotopes can be analyzed precisely without frequently constructing a reference frame through heated CO_2 gases. Our results provide a basis for optimizing IRMS performance for clumped isotope analysis.

1. Introduction

Clumped isotope, referred to as molecules containing two or more rare isotopes, constitutes a relatively new research field in geochemistry. Recently, clumped isotope compositions of carbonate (expressed as Δ_{47}, quantifying the excess abundance of CO_2 of mass 47 ($^{13}C^{18}O^{16}O$) in carbonate relative to theoretical random distribution, Eq. (1) below) have been employed as a powerful tool to elucidate paleotemperature quantitatively [1]. Clumped isotope thermometry has an advantage over the conventional oxygen isotope thermometry in cases where the isotopic composition of the formation water is not known. Therefore, the clumped isotope thermometer enables a more independent reconstruction of paleotemperature than the oxygen isotope thermometer. To date, this technique has been applied in many areas, such as elucidating body temperatures of some extinct vertebrates and dinosaurs [2,3], reconstructing changes in environmental temperatures during some key paleoclimate periods, like the last glacial maximum [4], Eocene–Oligocene transition period [5] and Paleocene–Eocene thermal maximum [6], or for constraining diagenetic alteration [7].

Despite the broad application of the clumped isotope thermometry, there are some experimental problems to be resolved, yet. One prominent problem lies in the data comparison among different laboratories. For example, the maximum difference in Δ_{47} values generated by various laboratories for the same carbonate substance in a recent inter-lab calibration reached up to 0.07‰ (Stefano Bernasconi, personal communication), corresponding to a temperature difference of roughly 15 °C or even more. Although the reasons for this large discrepancy remain unclear and may be manifold, the mass spectrometer itself could be an important aspect to be considered especially with a range of bulk $\delta^{13}C$ and $\delta^{18}O$ compositions. For measurements of Δ_{47} values, a dependence of the measured Δ_{47} on bulk $\delta^{13}C$ and $\delta^{18}O$ compositions (namely δ_{47}, a δ-notation of mass 47 of sample CO_2 gas relative to that of in-house laboratory reference gas) of CO_2 was observed in most laboratories. To correct for this nonlinearity between measured and real Δ_{47} values, a normalization is commonly adopted based on analysis of heated CO_2 gases over a range of bulk compositions. However, the slopes of the heated gas line results (HG line, results

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plotted as Δ_{47} vs. δ_{47}) determined by the same mass spectrometer varied over a relatively wide range from 0.0064 to 0.0128 for different time-periods [8]. This can introduce significant errors in Δ_{47} values if it is not precisely constrained in time and carefully corrected. In this case, we should frequently construct heated gas line to monitor changes in nonlinearity, which is tedious and time-consuming. The highly variable nonlinearity should be related to mass spectrometer configurations and needs to be investigated.

In this study, we performed a series of instrument parameter for enhancing the performance of our MAT253 isotope ratio mass spectrometer (IRMS). We recognized that the extraction potential of the IRMS ion source an important factor influencing accuracy and precision for measurements of CO_2 clumped isotope significantly. Moreover, under optimal extraction potential, we obtained a long-term invariant slope of the heated gas line, indicative of a relatively stable linearity for our mass spectrometer. This may provide a useful method for optimizing also other IRMS for clumped isotope analysis. To the best of our knowledge, no systematic research has been published on this topic.

2. Experimental

2.1. CO_2 extraction method

CO_2 gases liberated from NBS 19 (international calcite standard, distributed by the IAEA), Chinese national carbonate standards (GBW04405, GBW04406, GBW04417) and lab working standard LEVIG-CO-1 were analyzed for clumped isotopes. We extracted CO_2 from carbonates by reaction with anhydrous phosphoric acid, following the method of Ghosh et al. [1]. Briefly, about 15 mg of sample reacted with ~103% phosphoric acid (density 1.90 g/ml) under vacuum at a temperature of 25 °C for ca. 16 h (overnight). Product CO_2 was cryogenically purified via passing through three traps in sequence: a water trap immersed in liquid nitrogen + acetone slurry, an absorbent trap (filled with Porapak Q^{TM}, a divinyl benzene polymer) immersed in liquid nitrogen + ethylene glycol slurry and another water trap immersed in liquid nitrogen + acetone slurry, then collected into a small glass sample vessel using liquid nitrogen for determination.

2.2. Clumped isotope measurement

All analyses were carried out on a Thermo Finnigan MAT253 IRMS, which was configured to simultaneously collect ion beams at m/z 44, 45 and 46 (read through $3 \times 10^8\,\Omega$, $3 \times 10^{10}\,\Omega$ and $1 \times 10^{11}\,\Omega$ resistors), as well as 47, 48 and 49 (read through $1 \times 10^{12}\,\Omega$ resistors). The IRMS was operated with an electron energy of 84 V, an acceleration potential of ca. 9.5 kV, and with the 'variable ion source conductance (VISC)' closed. On this IRMS, we replaced the stainless steel capillary tubes with electroformed nickel (EFNi) capillaries, which would largely minimize isotope redistribution reactions [9]. The clumped isotope measurements were made in dual inlet mode, with an average beam intensity of 16 or 18 V on mass 44. Each analysis involves 8 cycles of sample-standard comparison and each cycle involves 26 s integration of sample and standard ion beams. Analyses were standardized by comparison with an intra-laboratory reference gas whose bulk isotopic composition had been previously calibrated against CO_2 produced by phosphoric acid digestion of NBS 19.

In this study, we reported the excess abundance of mass 47 using the Δ_{47} notation [10], which relates the measured isotopic ratios $R^{47}$of sample to the ratio R^{47^*} of the same sample if it had a stochastic isotope distribution. Δ_{47} is calculated as the following equation:

$$\Delta_{47} = \left[\left(\frac{R^{47}}{R^{47*}} - 1\right) - \left(\frac{R^{46}}{R^{46*}} - 1\right) - \left(\frac{R^{45}}{R^{45*}} - 1\right)\right] \qquad (1)$$

where R^{47},R^{46} and R^{45} are abundance ratios of masses 47, 46 and 45 relative to mass 44 (e.g., 47/44). R^{47^*}, R^{46^*} and R^{45^*} are the corresponding ratios that would occur in the same sample if it had a stochastic distribution. Theoretically, Δ_{47} for CO_2 is close to 0‰ at 1000 °C, which means a stochastic distribution is achieved. In practice, three or more heated CO_2 gases of different isotopic compositions with a large range of δ_{47} relative to the reference gas were carefully measured to construct a HG line (a δ_{47} vs. Δ_{47} plot), which is used to correct for non-linearity effects of mass spectrometry and to obtain the real Δ_{47} value [8]. The raw Δ_{47} of a sample was calculated using Eq. (1), but it is necessary to correct it for linearity effects in the IRMS, which were determined by the measurement of heated gases of different isotopic composition (i.e., HG line). The correction was performed following the procedures described by Schmid and Bernasconi [11].

2.3. HG line construction

In this study, carbonates with different isotopic compositions were used to construct an experimental HG line. These carbonates were GBW04405 ($\delta^{13}C_{VPDB}$: +0.57‰; $\delta^{18}O_{VPDB}$: −8.49‰), GBW04406 ($\delta^{13}C_{VPDB}$: −10.85‰; $\delta^{18}O_{VPDB}$: −12.40‰), GBW04417 ($\delta^{13}C_{VPDB}$: −6.06‰; $\delta^{18}O_{VPDB}$: −24.12‰), LEVIG-CO-1 ($\delta^{13}C_{VPDB}$: −46.81‰; $\delta^{18}O_{VPDB}$: −13.47‰) and NBS 19 ($\delta^{13}C_{VPDB}$: +1.95‰; $\delta^{18}O_{VPDB}$: −2.20‰). The ranges for $\delta^{13}C$ and $\delta^{18}O$ values of the above chosen carbonates normally cover those of natural carbonate samples we routinely measured. CO_2 gases were produced via phosphoric acid digestion of those carbonates, sealed in quartz-glass tubes and then heated to 1060 °C in a muffle furnace for 3 h and rapidly quenched in tap water at room temperature. Heated gases were purified using the cryogenic procedures in a manner identical to the preparation of samples before being transferred to IRMS.

3. Results and discussion

3.1. Optimization of instrument

To optimize the performance of our MAT253 IRMS, we first measured the reference gas (vs. itself) under different extraction potentials, which controls the residence time of CO_2 gas in the source. Fig. 1 shows values of Δ_{47} determined for the reference gases and distribution of internal precisions for clumped isotope analyses of the same gases with different extraction potentials. As can be seen, the average Δ_{47} for 90% extraction is 0.0014‰, very close to the expected value of zero (Fig. 1a). Meanwhile, the internal precisions of clumped isotope analyses for 90% extraction are better than those for other extraction potentials, e.g., smaller than 0.014‰ with most around 0.010‰ (Fig. 1b). Therefore, 90% extraction seems to be the optimum extraction potential for clumped isotope analysis using our IRMS. To be more specific, 90% extraction potential refers to the absolute potential of 9550 V for the 10 KV instrument of MAT253 with a full span of 500 V for the applied extraction. In another word, 90% extraction corresponds to 4.5% of the accelerating voltage. This indicates that the extraction potential of IRMS is an important factor governing accuracy and precision of clumped isotope analysis. The reason may be that the extraction potential can influence isotopic 'scrambling' in the ion source through controlling the ion residence time. For example, a