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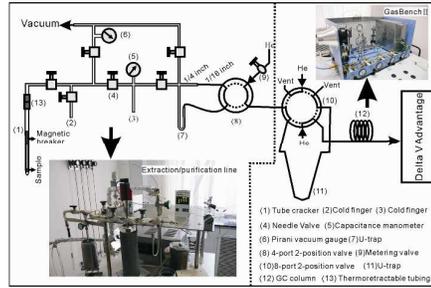
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Analyzing carbon isotope of CO<sub>2</sub> of fluid inclusions in minerals using decrepitation by sealed tube coupled to continuous-flow mass spectrometry.



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## Combination of a sealed-tube decrepitation with continuous-flow isotope ratio mass spectrometry for carbon isotope analyses of CO<sub>2</sub> from fluid inclusions in minerals

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A method was presented to perform carbon isotope analyses of CO<sub>2</sub> from fluid inclusions in minerals, using decrepitation by the sealed tube method followed by cryogenic separation of the resultant CO<sub>2</sub> in a high-vacuum line, coupled via GasBench II to a DELTA V isotope ratio mass spectrometry. The proposed method greatly reduces the sample size and the laboratory time without compromising the precision of the results.

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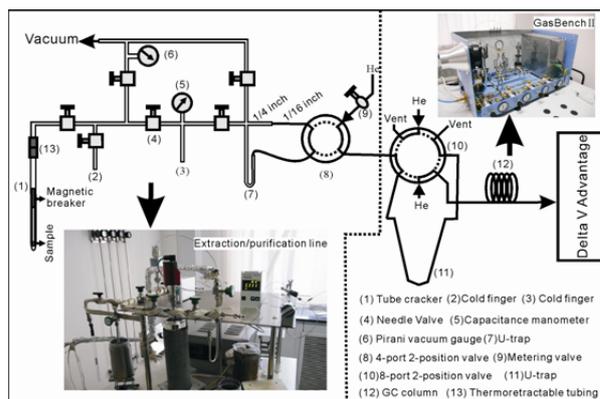
Fluid inclusions are small liquid- or vapor-filled vacuoles in minerals. Combined studies of stable isotopes and fluid inclusions in minerals that precipitated in different geological environments (e.g., magmatic, hydrothermal, and sedimentary) may provide valuable information regarding the origin, generation of these minerals<sup>1,2</sup>. CO<sub>2</sub> is a common component in fluid inclusions. Carbon isotope analysis of CO<sub>2</sub> found in inclusions may provide direct information concerning past geological processes<sup>3</sup>.

Conventional techniques for determination of carbon isotope of the CO<sub>2</sub> trapped in inclusions are based on off-line thermal decrepitation or vacuum crushing methods followed by dual-inlet mass spectrometric analyses<sup>3</sup>. The advantage of offline preparation coupled with the dual-inlet system is that good precision can be achieved, whereas the disadvantage is that a relatively large amount of CO<sub>2</sub> is needed, necessitating extraction from approximately 1 g (or even more) of sample material. In addition, due to the complex mixtures of various components of the sample gases in fluid inclusions, the precision of the carbon isotope analysis of CO<sub>2</sub> from fluid inclusions is poor. In recent years, the method of continuous-flow isotope ratio mass spectrometry (CF-IRMS) has been well developed. This technique was employed to transport the released gas in an inert gas stream directly to mass spectrometer. As a result, CF-IRMS allows utilization of much smaller sample amounts. Furthermore, the various components of the sample gas from fluid inclusions can be effectively separated in the gas chromatographic column in the continuous flow system. Based on continuous flow techniques, commercial continuous units, such as the Elemental Analyzer or continuous gas/chromatography (GC/C), have been modified for the analysis of the carbon isotope ratios of CO<sub>2</sub> in smaller samples<sup>4-6</sup>.

In the present paper, we demonstrate an off-line sealed tube decrepitation preparation method combined with continuous-flow isotope ratio mass spectrometry (CF-IRMS) using a Thermo Fisher GasBench II (GB II) unit (designed for automated carbonate and water analyses) as the inlet device leading to a mass spectrometer.

The sealed-tube method has been used for the analysis of hydrogen isotopes in H<sub>2</sub>O or hydrogen and carbon isotopes in organic matter<sup>7-9</sup>. In this study, the method was employed to release the volatiles from the fluid inclusions in the samples by thermal decrepitation. A quartz tube loaded with the sample was flame-sealed to produce an approximately 8-cm-long ampoule and was placed into a resistance furnace heated to 600°C for 15 min. In contrast to conventional decrepitation in a tube furnace, the

advantage of this method is that a batch of samples can be decrepitated in the resistance furnace at the same time.



**Fig. 1** Schematic diagram and photographs of the high-vacuum line and interface with the GasBench II.

To transfer the released gases into the continuous flow system, we designed a metal, low-blank vacuum extraction/purification line, which was built at the Institute of Geology and Geophysics of the Chinese Academy of Sciences. The high-vacuum line also includes an interface built for the transfer of small samples of CO<sub>2</sub> into the GB II in a He stream, as is illustrated schematically in Fig. 1. The design is similar in several ways to those constructed for analyses of nanomolar quantities of N<sub>2</sub><sup>10</sup>. The vacuum line was composed of a 1/4 inch stainless steel (ss) tube and a needle valve (Swagelok Inc.). In addition, to release the volatiles from the sealed tube, we designed a tube cracker device made of a quartz tube (12 mm OD×25 cm, closed on one end). Following the decrepitation of the samples, the sealed tube was loaded into the cracker tube, which was connected to the vacuum line with a magnetic breaker (Fig. 1).

The vacuum extraction/purification line was coupled with a Thermo GasBench II carrier-gas system through a Valco type valve (VICI inc; 4 port 2-position valve) with a He stream system (Fig. 1). Furthermore, we have modified the configuration of the GB II somewhat to allow the use of a U-trap (7, 1/16-inch ss tubing, Fig. 1) for transferring CO<sub>2</sub> from our extraction/purification line into the GB II. The main modification is that we have substituted the aliquoting loop attached to the main Valco valve with the U-trap (11 on Fig. 1) to transfer the CO<sub>2</sub> samples from our vacuum line into the GB II. In the GB II system, a porous layer open tubular (PLOT) fused silica chromatographic column PoraPLOT Q 25x0.32 (Varian MD-24-12-1) is held at 50°C for effective separation of the various components of the sample gas. An isotope-ratio mass spectrometer (Thermo Fisher Delta V Advantage) with GB II is employed to couple sample and reference CO<sub>2</sub> flow via two open

splits, and to analyze the isotope ratio of CO<sub>2</sub> in conjunction with software ISODAT 3.0.

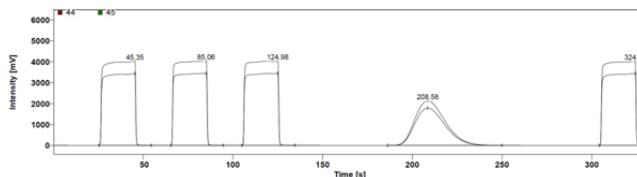
All carbon isotope results are reported against VPDB (Pee Dee Belemnite). The isotope ratios of carbon was represented by the  $\delta$ -notation:

$$\delta^{13}\text{C}(\text{‰}) = \left[ \left( \frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}} \right)_{\text{sample}} / \left( \frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}} \right)_{\text{VPDB}} - 1 \right] \times 1000.$$

In the absence of a well-determined and internationally accepted fluid inclusion standard, the precision and accuracy of the method can be estimated by analyzing IAEA-CH-6 (Sucrose,  $\delta^{13}\text{C} = 10.45 \pm 0.04$ , VPDB) and IAEA-CH-7 (Polyethylene foil,  $\delta^{13}\text{C} = -32.15 \pm 0.05$ , VPDB). To analyze a “real” sample in this study, we chose a quartz sample (zk104-90, donated by Ping Shen, IGGCAS) which was collected from the quartz–chalcopyrite veins of the porphyry copper deposits in Xinjiang Province. The gas composition of the sample mainly consists of CO<sub>2</sub>, CH<sub>4</sub> and other gases (personal communication with Ping Shen).

Ca. 100 mg of the sample (zk104-90, ca. 50 mesh) was placed into quartz tubes (6 mm OD×16 cm, closed on one end) that were previously combusted in atmosphere at 900°C for 12 h to remove organic and other contaminants. Along with 0.5 g of the CuO reagent, the international references IAEA-CH-6 and IAEA-CH-7 were placed into quartz tubes (8 mm OD×20 cm, closed on one end). The quartz tubes with the sample and the standards were then attached to another vacuum line composed of a glass tube and pumped for at least half an hour at  $<10^{-2}$  Pa. After evacuation, the quartz tubes were flame-sealed to produce 8-cm-long ampoules and were placed into a furnace set to 600°C for 15 minutes (for the mineral sample) and 850°C for 4 h (for IAEA-CH-6 and IAEA-CH-7). Then, the sealed quartz tubes were placed into the cracker tube, which was fitted vertically to the vacuum line (Fig. 1). After the whole extraction/purification line was evacuated to a vacuum level lower than  $10^{-2}$  Pa, we cracked the sealed quartz tube, which led to the volatiles being liberated (Fig. 1). To remove the released water, the cold finger (3, Fig. 1) was placed in a mixture of alcohol and liquid N<sub>2</sub>. After the trap for H<sub>2</sub>O was assumed to be complete, when no decrease in pressure was observed with a capacitance manometer, the U trap (7, Fig. 1) was placed into liquid N<sub>2</sub> to collect the released gases. After the transfer of the gases, liquid N<sub>2</sub> was removed from the trap (7, Fig. 1), and the gases were released again. The final procedure in the vacuum line is to change the position of the 4-port 2-position valve. To prevent the back-diffusion of the atmosphere into the GB II system, the meter valve was used to control the optimal He Gas flow rate (4, Fig. 1) before changing the position of the 4-port 2-position valve. Next, the He stream was flushed into the U-trap (7, Fig. 1), and it carried the

released gases into the U-trap (11, Fig. 1) in the GB II system (Fig. 1). Using the ISODAT program for the GB II, the carbon isotope of CO<sub>2</sub> was analyzed through mass spectrometer.



**Fig. 2** Signal intensity trace of *m/z* 44 and 45 after flow of gases from fluid inclusions in the quartz sample (zk104-90).

The first three and the last peaks presented in Fig. 2 are the reference gas peaks for CO<sub>2</sub>, and the fourth peak is the CO<sub>2</sub> peak of the natural gas released from the fluid inclusion by thermal decrepitation. <sup>13</sup>C/<sup>12</sup>C ratios were measured in the gases relative to a working standard CO<sub>2</sub> gas (99.999%; Beiwen Gas Corp., Beijing, China), which was calibrated against VPDB using the international carbon isotope standard NBS19 (Limestone,  $\delta^{13}\text{C} = +1.95\text{‰}$ , VPDB). The international references IAEA-CH-6 and IAEA-CH-7 that monitor the whole analysis procedure show good precision (0.09‰, 0.07‰, 1 $\sigma$ ), indicating that the whole analysis procedure is reliable. The analyzed average  $\delta^{13}\text{C}$  values of IAEA-CH-6 and IAEA-CH-7 show values that are heavier than those of the recommended values. The offsets (0.49‰ and 0.38‰) were used to correct the values of the samples.

The  $\delta^{13}\text{C}$  values of gases released from fluid inclusions are shown in Table S1† with a precision of 0.6‰. The excellent reproducibility of the  $\delta^{13}\text{C}$  values for CO<sub>2</sub> indicates complete gas separation. In addition, by subtracting the offset between the measured values and the given values of IAEA-CH-6, we obtained the corrected values of the samples (-12.01‰, VPDB).

Compared to the conventional tube furnace decrepitation method coupled to a dual inlet analysis, the method described here can save significant sample preparation time. In fact, primarily due to the use of the quartz tube decrepitation, a batch of samples (nine samples) can be simultaneously decrepitated in 15 min. Thus, 120 minutes can be saved for the decrepitation of all nine samples. In addition, due to the use of the continuous flow technique, the sample size (100 mg) can be lowered by approximately an order of magnitude relative to the conventional method (1000 mg). Using GasBench II coupled to isotope ratio mass spectrometry, for measuring CO<sub>2</sub> smaller than 100 nmol, the precision of measurements deteriorates rapidly and becomes unacceptably large for most interpretations of isotopic compositions<sup>11</sup>. Therefore, in order to get

high-precision carbon isotope results (< 0.1‰), lower limit for measuring CO<sub>2</sub> should be 100 nmol<sup>11,12</sup>.

## Conclusions

This paper presents a coupled extraction and <sup>13</sup>C/<sup>12</sup>C analysis procedure for CO<sub>2</sub> from inclusions in minerals. This approach uses off-line decrepitation by the sealed tube method followed by cryogenic separation of the resultant CO<sub>2</sub> in a high-vacuum line, coupled to continuous-flow mass spectrometry to measure the <sup>13</sup>C/<sup>12</sup>C ratio. The application of this method was demonstrated for two international standards (IAEA-CH-6 and IAEA-CH-7), exhibiting excellent reproducibility and precision for the ratios of <sup>13</sup>C/<sup>12</sup>C in samples with fluid inclusions. In addition, the measurement of a real sample that contains inclusions (zk104-90) indicates good reproducibility (0.6%), reflecting the good separation of the mixing gas through the GC column in GB II. The proposed method greatly reduces the sample size and the laboratory time without compromising the precision of the final results.

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