

A new SF₆ inlet system with a modified Faraday collector alignment of Finnigan MAT-251 mass spectrometer for sulfur isotope measurement

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Abstract A new inlet system for the preparation of SF₆ gas by fluorination of sulfide minerals, suitable for both *in-situ* laser ablation and powder samples, was connected to the existing CO₂ inlet system of the Finnigan MAT-251 mass spectrometer at Shizuoka University. The preparation line is composed of a fluorine generator, two types of reaction chambers, capacitance manometer, KBr canister and liquid nitrogen slush connected by pneumatic bellows valves. It also includes a working standard SF₆ gas reservoir and a machine standard SF₆ gas reservoir for routine analyses. The preparation line can hold high vacuum conditions without appreciable leaks for intervals more than that required to complete one sample measurement. For simultaneous measurement of [127], [128], [129] and [131] isotopes of SF₅⁺, we have renovated Faraday collectors by reducing its body thickness from 4.5 mm to 3.5 mm and realigned the collector configuration of the mass spectrometer. Preliminary results of δ³⁴S values for working standard SF₆ gas gave high precession of ±0.003‰. Further modifications in the collector assembly are in progress for the simultaneous measurement of the closely spaced ion trajectory of [127], [128] and [129] isotopes of SF₅⁺.

Key Words: sulfur isotopes, inlet system, SF₆, Faraday collector, laser ablation

Introduction

Conventional measurement of sulfur isotopes are carried out using SO₂ gas in a gas source mass spectrometer (Hoefs, 1997). However, recently, SF₆ gas has been recognized to have several advantages over SO₂ for sulfur isotope analysis (Rees, 1978, Rumble *et al.*, 1993; Hu *et al.*, 2003; Ono *et al.*, 2006). One of these advantages is that fluorine, having only a single isotope, does not produce any isobaric interferences and SF₆ can obtain reliable data even for the rarer isotopes of ³³S and ³⁶S, in addition to the more abundant ³²S and ³⁴S. Furthermore, small quantities of SF₆ gas are easy to handle without isotopic fractionation because the gas is condensable in liquid nitrogen cold trap, is chemically inert, does not adsorb in the inner surfaces of vacuum lines, and is insensitive to moisture. Rumble *et al.* (1993) and Hu *et al.* (2003) described the method of laser heating of sulfide minerals in a fluorine atmosphere for high spatial resolution *in-situ* analyses with a precision and accuracy comparable to that of conventional fluorination analyses of powdered samples.

The Finnigan MAT-251 dual inlet gas source mass spectrometer at Shizuoka University (Fig. 1) was originally designed to measure carbon and oxygen (as CO₂), sulfur (as SO₂) and nitrogen (as N₂) isotopes and was routinely set up for the measurement of carbon and oxygen isotopes using carbon dioxide (Wada *et al.*, 2008). Here we report a new inlet system for the preparation of SF₆ gas as a medium for sulfur isotope analysis using Finnigan MAT-251 mass spectrometer. We have also renovated the Faraday collector and modified the collector alignment of the mass spectrometer, in order to measure the closely spaced ion trajectory of [127] (³²SF₅⁺), [128] (³³SF₅⁺), [129] (³⁴SF₅⁺) and [131] (³⁶SF₅⁺) isotopes of SF₆ gas. Finally, we discuss the accuracy of the measurement of δ³⁴S values for working standard SF₆ gas using the new system.

SF₆ inlet system

The structure of the SF₆ inlet system is based on the laser fluorination system mentioned in Hu *et al.* (2003) and has many similarities to the laser fluorination oxygen isotope

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analytical system at Shizuoka University (Matsui *et al.*, 2003). The new inlet system was linked to the existing CO₂ gas inlet system of the Finnigan MAT-251 mass spectrometer (Wada *et al.*, 2008) and is schematically illustrated in Figure 2.

The vacuum line was constructed using 3/8" stainless steel pipes, Swagelok® joints and Cajon® pneumatic bellows valves (Fig. 3A), except for the fluorine generator and reaction tubes that are made of nickel. The line is evacuated using a combination of turbo pump (PFEIFFER® TPHODN40KF) and two rotary pumps. There are four pressure gauges (P₁-P₄) located at different segments in the line. P₁, P₂ and P₃ are pirani gauges (WAKAIDA® PG-2B) in the pre-existing CO₂ inlet system and P₄ is a newly added capacitance manometer (PFEIFFER® CMR362) (Fig. 3A). Altogether the system is composed of twenty eight Cajon® pneumatic bellows valves, controlled by computer using a C++ program connected through two GPIB controllers. In addition, there are two manual valves (M₁ and M₂), which are used to keep the fluorine generator and waste bromine trap closed during their removal for addition of the reagent and disposal of waste bromine, respectively.

There are five liquid nitrogen cold traps (T₉-T₁₃) in the SF₆ preparation line (Fig. 2B). These cold traps are capable of condensing Br₂ and SF₆ gases, whereas F₂ gas is non-condensable. T₉ is made of stainless steel and designed to condense SF₆ gas formed by the reaction of sample with F₂ gas (Fig. 3C). T₁₀ and T₁₁ are single loop 3/8" stainless pipes (Fig. 3C) that condense Br₂ gas produced by the reaction of the un-reacted F₂ gas with KBr, while T₁₂ is waste Br₂ reservoir made of Kel-F® for temporary storage. F₂ gas is hazardous and highly reactive with moisture, and hence the un-reacted F₂ gas has to be disposed as solid KF by reacting with KBr. T₁₃ is a double loop 3/8" stainless steel cold trap (Fig. 3B), filled with steel wool for increasing the surface area of trapping. This cold trap condenses gas impurities that are generated from the fluorine reservoir.

Fluorine generator is made of nickel tube (1 inch in diameter; Fig. 3E) and contains the reagent potassium hepta fluoronickelate (K₂NiF₆ • KF). Fluorine generator is heated up to 350°C using a mantle heater to generate F₂ gas and gas pressure is monitored using the capacitance manometer (P₄) (Fig. 2B). Three stainless steel sintered 2 µm filters are included to restrict the movement of fine particles of K₂NiF₆ • KF, KBr or KF during evacuation.

The inlet system is designed for the preparation of SF₆ gas from sulfide samples in two different ways. 1) Laser ablation: Laser ablation of polished sulfide minerals is carried out *in-situ* inside a reaction chamber (RC₁), which is made of stainless steel and has a BaF₂ window for uninterrupted laser passage and to observe the progress of lasing on the sample surface (Fig. 4A). A high magnification camera is connected with the monitor (KEYENCE VH-6300) to observe the progress of the reaction during laser

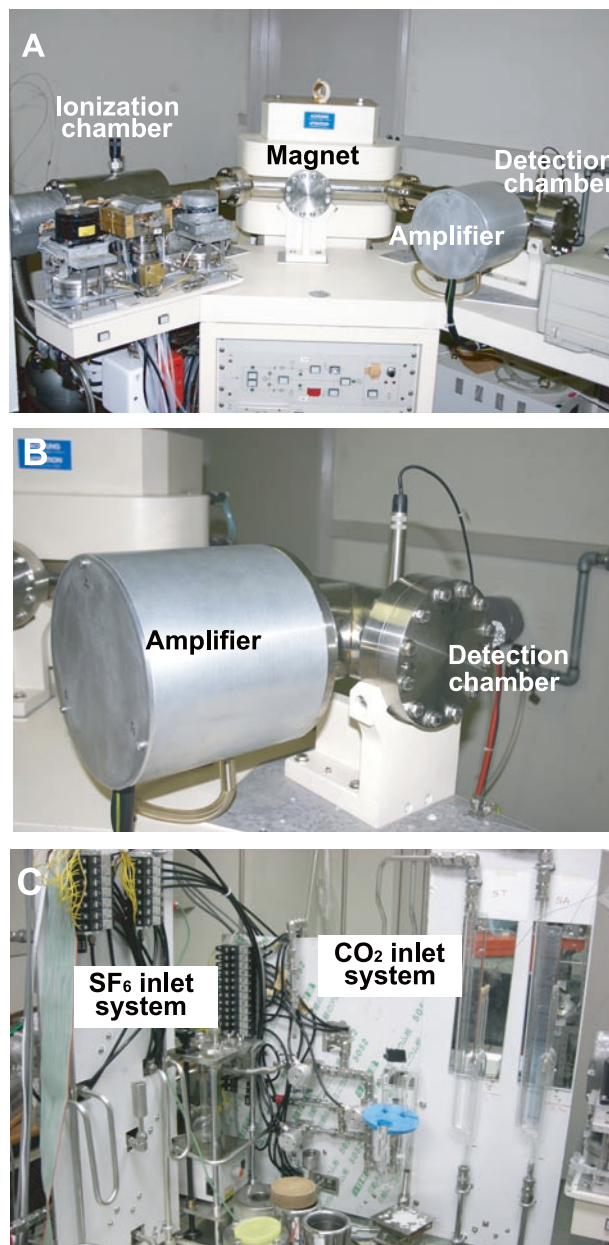


Fig. 1 (A) Generalized view of the Finnigan MAT-251 mass spectrometer. (B) The detection chamber and amplifying unit. (C) Front view of the inlet systems for CO₂ and SF₆.

ablation. 2) Powder samples: Nickel reaction tubes (RC₂) are used for the preparation of SF₆ gas from powdered samples. The capacitance manometer (P₄), with a scale range of 100 to 0.1 mbar, a resolution of 0.1 mbar and an accuracy of 0.5% of scale reading, is used for monitoring the F₂ gas pressure inside both reaction chambers. Residual F₂ gas that is remaining in the reaction chamber after the reaction with sulfide mineral is passed over heated KBr (~200°C) (Fig. 3D) to form KF (solid) and Br₂ (vapor). Br₂ vapor is stored in T₁₂ waste reservoir (Fig. 3A).

Two standard SF₆ gas reservoirs, having a volume of one liter each, one for working standard (WSTD) and other for

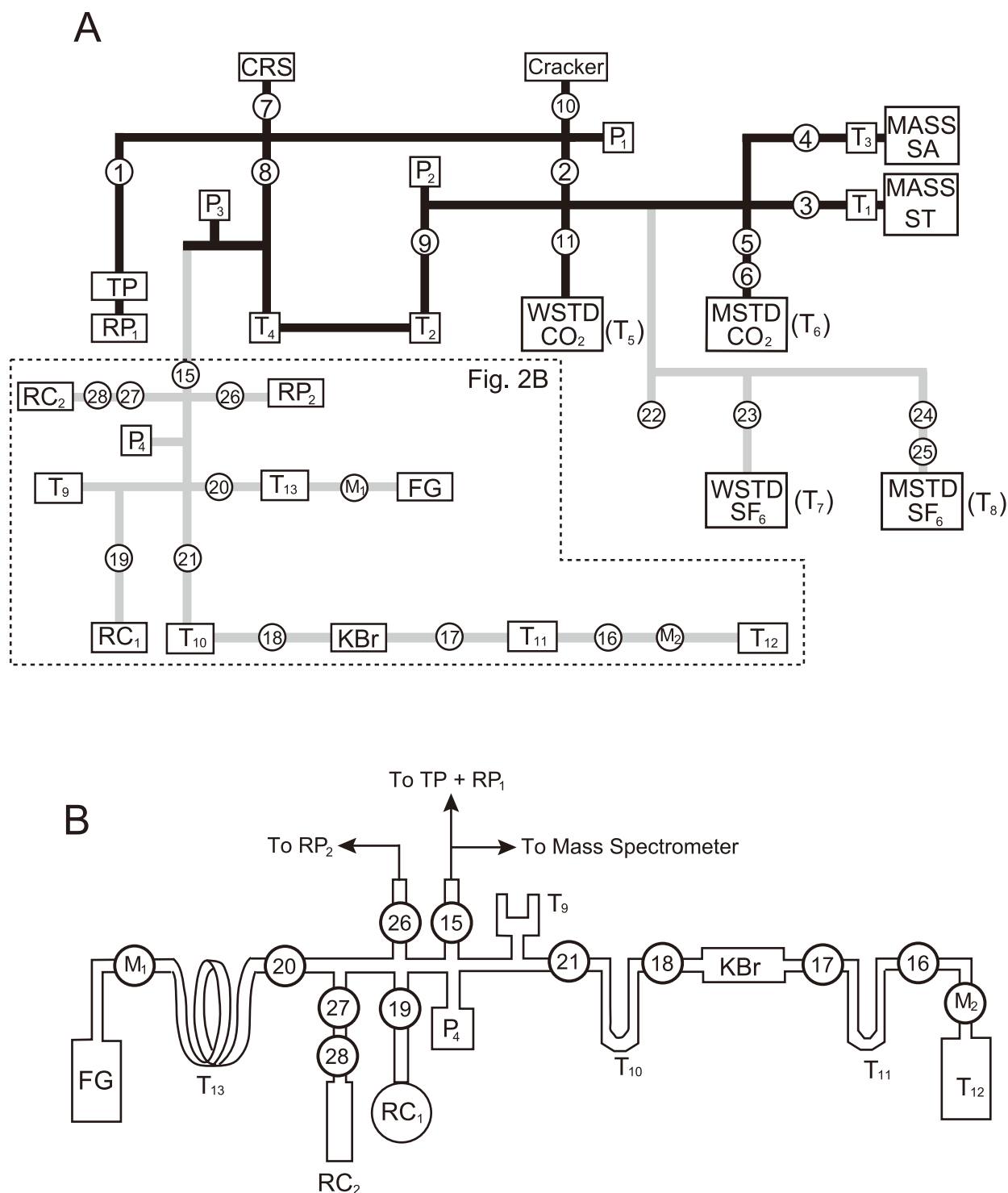


Fig. 2 (A) Schematic layout of the vacuum line for CO₂ and SF₆ inlet systems connected to the Finnigan MAT-251 mass spectrometer. Black lines correspond to the inlet line for CO₂ (Wada *et al.*, 2008) and grey line is the newly constructed inlet line for SF₆. (B) Schematic view of the SF₆ preparation system. Abbreviations are; CRS: Carbonate reaction system; FG: Fluorine generator; KBr: Canister for conversion of residual F₂; M₁, M₂: Manual valves; MASS SA: Capillary connection of sample gas to ionization chamber; MASS ST: Capillary connection of standard gas to ionization chamber; MSTD: Machine standard gas reservoir; P₁~P₃: Pirani gauge sensors; P₄: Capacitance manometer; RC₁: Reaction chamber for laser ablation; RC₂: Reaction tubes for powder samples; RP₁, RP₂: Rotary pumps; T₁~T₃, T₉~T₁₃: Liquid nitrogen traps; T₄: Pentane slush; TP: Turbo pump; WSTD: Working standard gas reservoir. Numerals 1 to 28 represent pneumatic bellows valves.

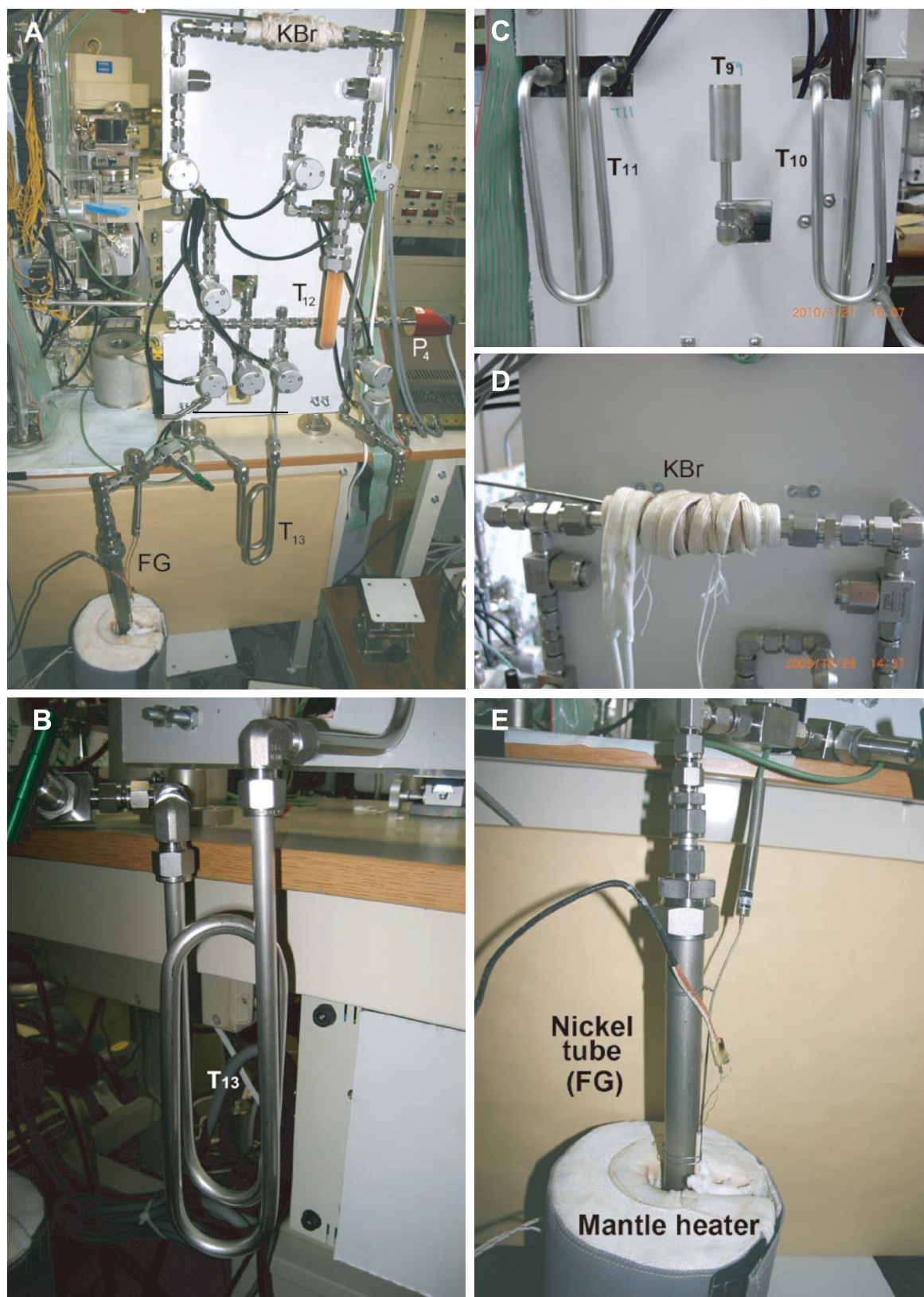


Fig. 3 (A) Photograph showing the rear view of the SF_6 line. (B) Double loop stainless steel cold trap T_{13} used for trapping condensable impurities released from the fluorine generator. (C) Liquid nitrogen cold traps (T_9 , T_{10} and T_{11}) used in the SF_6 line. T_9 is used for trapping SF_6 produced from samples during fluorination while T_{10} and T_{11} traps the Br_2 vapor produced from unreacted F_2 gas in the KBr canister. (D) KBr for the conversion of excess fluorine to solid KF and Br_2 . Two filters ($2\ \mu\text{m}$) are connected on both sides of the canister to prevent the movement of fine powder from the canister. (E) Fluorine generator (FG) made of nickel. This generator contains $\text{K}_2\text{NiF}_6 \cdot \text{KF}$, which generates fluorine when the temperature is increased to 350°C and a reverse reaction occurs at a temperature of around 200°C . The temperature is increased using a mantle heater.

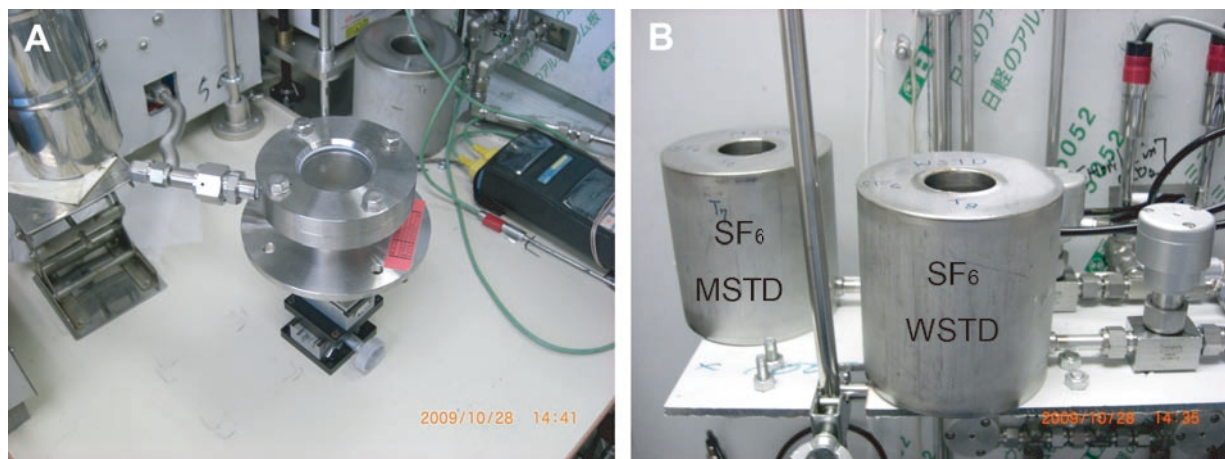


Fig. 4 (A) Reaction chamber for laser ablation to generate SF₆ from polished sulfide samples. BaF₂ window in the reaction chamber allows the laser beam to pass through and also allows the inside view during laser ablation. The reaction chamber is placed on an X-Y stage. (B) Working standard (WSTD) and machine standard (MSTD) gas reservoirs containing SF₆ gas.

machine standard (MSTD), were also connected to the inlet system (Fig. 4B). These reservoirs were filled with commercially produced SF₆ gas with a purity of 99.999% (Kanto Denka Kogyo Co., Ltd.). WSTD is used as a laboratory standard gas during routine measurements, whereas a small portion of MSTD gas is measured as a sample gas twice, in the beginning and in the end of the day of measurement, to confirm the stability of mass spectrometer.

Vacuum condition

Initial vacuum tests of the system were carried out in order to determine whether the newly built system can withstand high-vacuum condition for intervals of time required for the preparation and analysis of a sample. The system was evacuated to the minimum pressure measured at the capacitance manometer (P₄) and vacuum check was conducted based on the following procedure. Initially, all the valves were kept closed for a specific time (*e.g.*, 5 hours) and then, starting from the valve nearer to P₄, valves were opened one by one, while reading the shift in P₄ values. For example, in the case of reaction chamber segment's vacuum check, it is kept in the closed condition with the valve No. 19 closed and No. 15 opened. Subsequently, valve No. 15 is closed and No. 19 is opened and the shift in P₄ value is measured. Similarly, all segments of the system were tested at specific time intervals and the relation between the time and the shift in P₄ reading for each segment of the vacuum line is shown in Fig. 5. It was found that all segments in the line can essentially keep high vacuum condition for more than 30 minutes, the maximum time required for the preparation of one sample. The reaction chamber lost its high vacuum condition when it is closed for longer than 10 hours. This is possibly due to its large internal

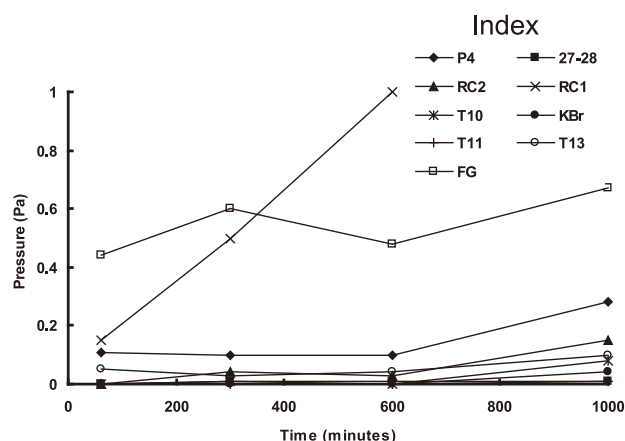


Fig. 5 Results showing the segment wise leak check for the SF₆ inlet line plotted as a function of pressure (Pa) measured at P₄ with time. Abbreviations (same as in Fig 2) represent the segments that connect the segment with P₄ in the vacuum line.

volume and minute leaks along the large 'O' rings used in the sample exchange lid.

Modifications in Faraday collector settings

The Finnigan MAT-251 mass spectrometer at Shizuoka University has six built-in Faraday collectors. The Faraday collectors are arranged parallel to each other inside the ion detector housing as shown in Fig. 6A and 6B. Faraday collector comprises of a rectangular stainless steel holder covered by thin stainless steel plates, in which the "Faraday cup" is fixed in a ceramic holder for insulation (Fig. 6C and 6D). The original thickness of the collector is 4.5 mm.

The amplifier housing comprises of six amplifiers (Fig. 6E and 6F) which are connected to the collector terminal through silver cables (Fig. 6A). Though six collectors and

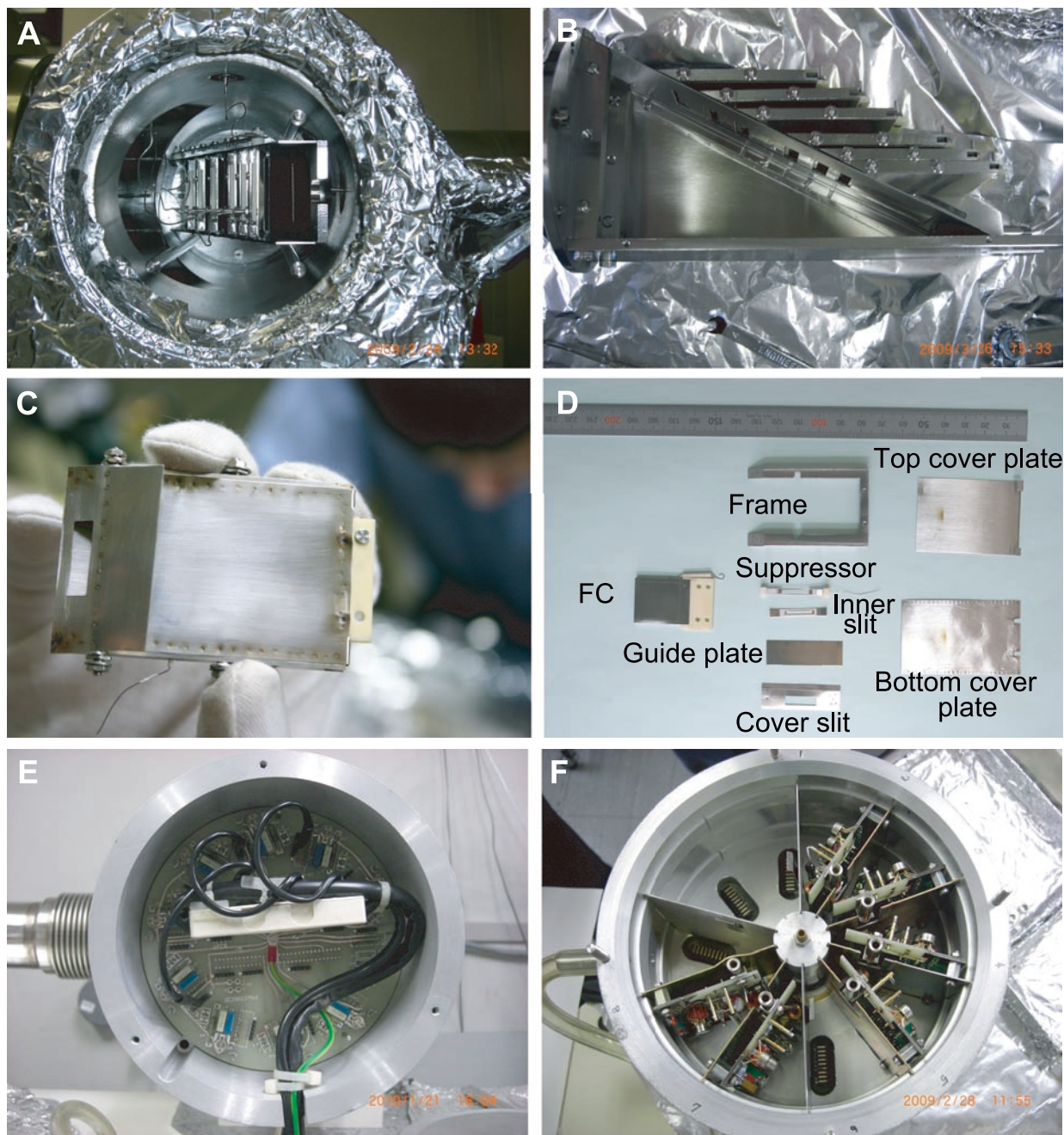


Fig. 6 (A) General view of the Faraday collector assembly inside the detector chamber of the MAT-251 mass spectrometer. (B) The arrangement of six collectors, in which collectors 4, 5 and 7 were used for detecting the CO_2 ions. (C) Enlarged view of a single collector. (D) Disassembled parts of a Faraday collector (FC). The thickness of the frame was reduced from 4.5 mm to 3.8 mm and reassembled by spot welding with new cover plates. (E) Exterior view of the amplifying unit of the MAT-251 mass spectrometer. (F) The arrangement of resistors inside the amplifying unit.

resistors are present, only three collectors can be simultaneously measured by the MAT-251 mass spectrometer, because the computer program (ISODAT) controlling system is designed to work with only three voltage frequency converters.

The initial setup of the collector assembly of the MAT-251 mass spectrometer was to detect the CO_2^+ ions of mass

[44], [45] and [46] (Fig. 7A). An accelerating voltage of 7980 V was used for the measurement with collector number 4, 5 and 7 connected to resistors 300 M Ω , 30 G Ω and 100 G Ω , respectively. The space between the collectors is fixed so that all three ions can be detected simultaneously. The ion trajectory of the required isotopes is controlled by the accelerating voltage and magnetic field. Since sulfur

isotopes are measured using SF₅⁺ ions with mass numbers [126], [127], [129] and [131], the ion beam trajectories are situated close to each other, when compared with CO₂⁺ ions. Because the collectors were designed for lower mass numbers (<66 for SO₂) the collector thickness does not permit measurement of [126], [127] and [129] ions simultaneously. Therefore we decided to reduce the thickness. As a test, one collector (No. 2 in Fig. 7A), which was not used for CO₂ measurements, was removed from the collector assembly and its body thickness were reduced by about 1.0 mm. Furthermore, the slits in the collector shield, which is a stainless steel plate at the entrance of the collector assembly, were also modified to suite the position of the collectors for SF₆. The modified position of the collector is shown in Fig. 7B.

Mass scanning, termed B-SCAN, is used to identify the peak positions of the ions detected in each collector. An example of the B-SCAN obtained for the working standard SF₆ gas is illustrated in Fig. 8, shows the peaks of ions detected by the collector. The accelerating voltage was 3980 V. Collector nos. 2 and 3 were connected with resistors 10 GΩ and 300 MΩ, respectively, for detecting [129] (³⁴SF₅⁺) and [127] (³²SF₅⁺).

Measurement of working standard SF₆ gas

Initial tests were carried out using WSTD-SF₆ gas δ for determining the precision of sulfur isotope measurement using a modified collector assembly of Finnigan MAT-251. Same WSTD-SF₆ gas was introduced to the ionization

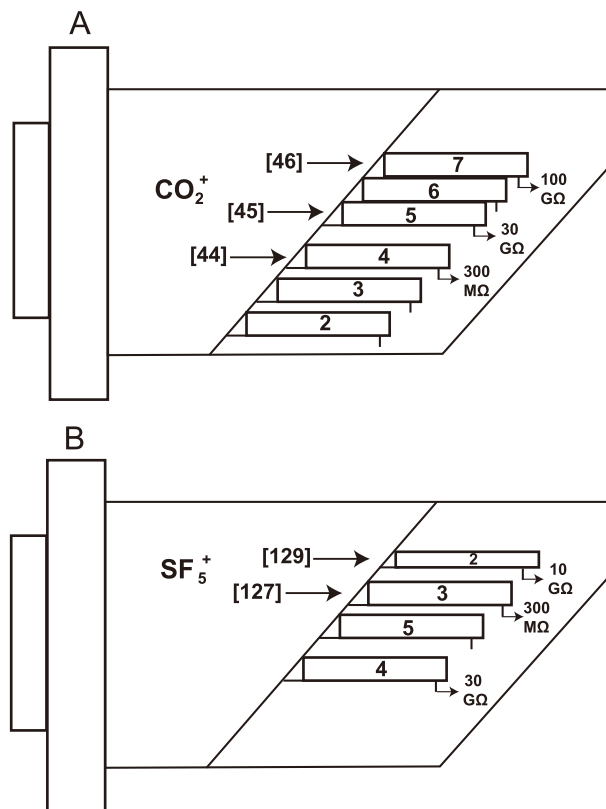


Fig. 7 (A) Schematic view of the collector assembly for the measurement of CO₂⁺ ions. Numerals indicate the collector number and those within parentheses represent mass number. The collectors connected with resistors were used for measurements. (B) Schematic view of the modified position of Faraday collectors for carbon and oxygen isotope measurements using CO₂ and sulfur isotope measurements using SF₆. The resistor in the amplifying unit for the collector 2 has to be changed from 100 GΩ to 10 GΩ for measuring δ³⁴S.

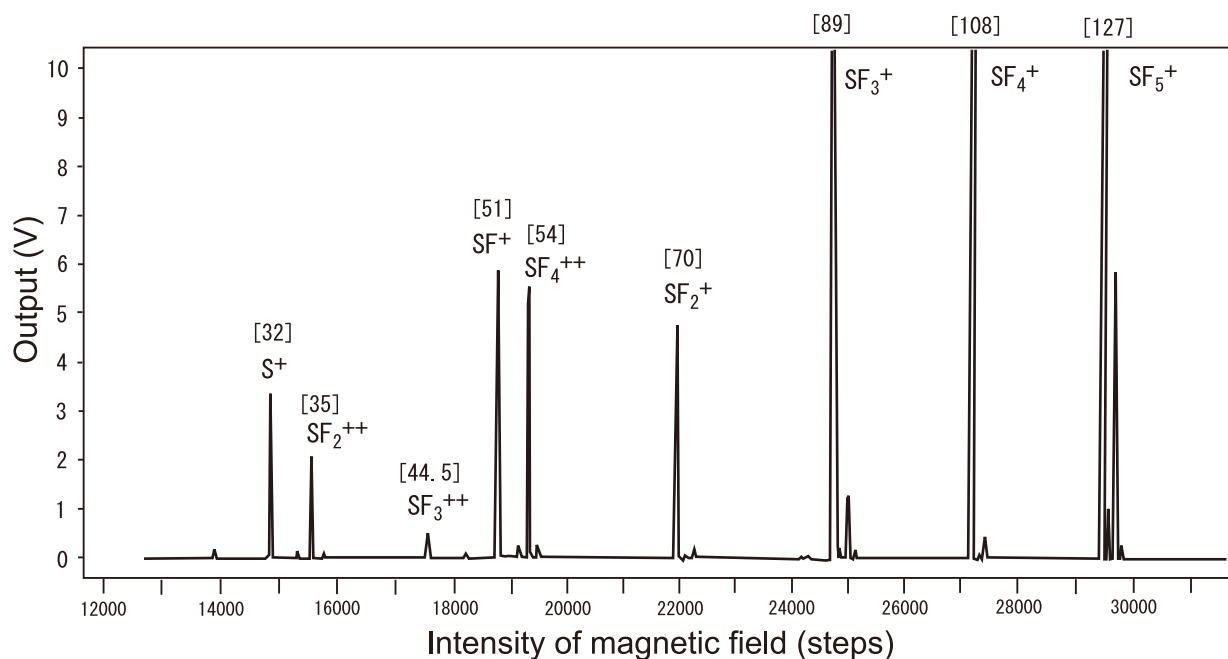


Fig. 8 The full range of mass spectrum obtained by the “B-SCAN” of WSTD SF₆ gas at a high voltage of 3980 V. The abscissa represents the magnetic field and the ordinate the output (V) measured in a single Faraday collector.

chamber through standard and sample capillary tubes (MASS ST and MASS SA in Fig. 2A) with a gas pressure of 100 mmHg and $\delta^{34}\text{S}$ values were observed continuously. The result is shown in Figure 9. The average of the raw data is $0.070 \pm 0.016\text{‰}$ (1σ ; $n = 60$), which shows very good precision. Further, the same experiment was carried out under varying gas pressures at 80 mmHg, 100 mmHg and 120 mmHg (Fig. 10). The average of $\delta^{34}\text{S}$ values are $0.003 \pm 0.011\text{‰}$ (1σ ; $n = 20$), $-0.003 \pm 0.011\text{‰}$ (1σ ; $n = 20$) and $0.005 \pm 0.015\text{‰}$ (1σ ; $n = 20$), for 80 mmHg, 100 mmHg and 120 mmHg, respectively. Because the capillary tube was cleaned by baking (see Wada *et al.*, 1984 for procedure of baking of capillary tube), the $\delta^{34}\text{S}$ values of this experiment had a better precision than the long term measurements. Considering that the error for single measurement within each population was lowest for 100 mmHg, we have chosen it as the best condition for the flow of SF_6 gas to the ionization chamber.

Concluding remarks

A new inlet system was constructed and installed to the MAT-251 mass spectrometer for the preparation and analyses of sulfur isotopes using SF_6 gas. The vacuum line holds high vacuum for time intervals required for the preparation of SF_6 gas from sulfide minerals. Faraday collector was renovated to suite the measurement of sulfur isotopes and the position of collectors was determined. Preliminary measurements of working standard SF_6 gas gave high precision. Further modifications for the measurement of all four isotopes of sulfur are in progress.

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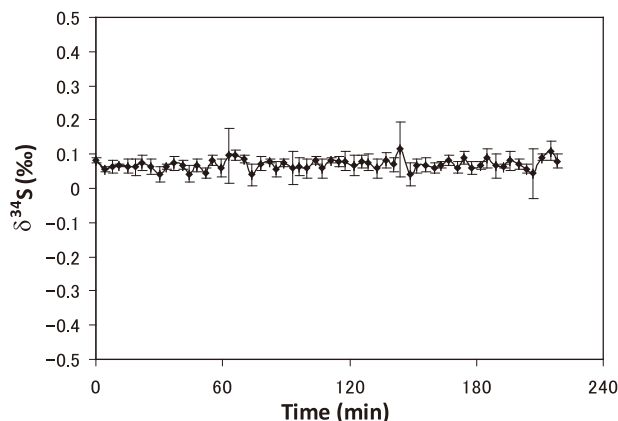


Fig. 9 Continuous measurement of working standard SF_6 gas showing the relation between $\delta^{34}\text{S}$ values and time. The average is $0.070 \pm 0.016\text{‰}$ (1σ ; $n = 60$). The measurement was carried out at a gas pressure of 100 mmHg with a gas volume of ~4ml in both standard and sample sides. Error bars represent standard deviation for four measurements of standard and sample gas.

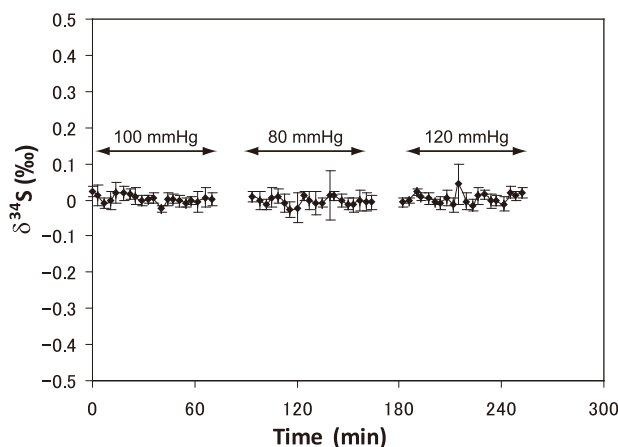


Fig. 10 Variation in $\delta^{34}\text{S}_{\text{WSTD}}$ values with time for WSTD SF_6 gas at three different pressure conditions. The first group of values was measured at 100 mmHg, the second group of values at 80 mmHg and the last group at 120 mmHg. Error bars represent standard deviation for four measurements of standard and sample gas.

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