

A Simple and Fast Separation Method of Fe Employing Extraction Resin for Isotope Ratio Determination by Multicollector ICP-MS

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ABSTRACT

A new, simple and fast separation method for Fe using an extraction chromatographic resin, Aliquat 336 (commercially available as TEVA resin) has been developed. A one milliliter column containing 0.33 mL TEVA resin on 0.67 mL CG-71C was used. Iron was adsorbed with $6 \text{ mol}\cdot\text{L}^{-1} \text{ HCl} + \text{H}_2\text{O}_2$ on TEVA resin, and recovered with $2 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$. The recovery yield and total blank were $93.5 \pm 6.5\%$ and 6 ng, respectively. The separation method is simple, and takes <2 hours. For evaluation of the Fe separation, Fe isotope ratios were measured by a double-spike method employing multicollector inductively coupled plasma source mass spectrometry (MC-ICP-MS) with repeatability of 0.06‰ (SD) for the standard solution and ~0.05‰ for the silicate samples. Therefore, the column chemistry developed in this study is a viable option for Fe isotope ratio measurement by MC-ICP-MS.

Keywords: Fe Separation; Fe Isotope Ratio; Multicollector Inductively Coupled Plasma Source Mass Spectrometry

1. Introduction

Triethylmethylammonium chloride (Aliquat 336) works as an anion exchanger, and is used in extraction chromatography (commercially sold as TEVA resin) [1]. Yang and Pin [2] and Grahek and Macefat [3] have tried to use the TEVA resin for Fe separation. The eluent volumes of 60 mL for 1 mL of the TEVA resin and 120 mL for 3 g (equates ~2.7 mL) TEVA resin were used, respectively. However, these volumes are too many to handle; large space is required and evaporation takes a long time. Recently, Makishima and Nakamura [4] successfully purified Zn using a one milliliter column composed of 0.33 mL TEVA resin on 0.67 mL CG-71C resin. They used the advantage of acid resistance of the TEVA resin [5], namely, HNO_3 was used in the final step to recover Zn that was strongly adsorbed on the resin. Based on this novel finding, it was noticed that the anionic character of the TEVA resin could be applied to separation of Fe. This study applies the TEVA resin for purification of Fe for isotope ratio measurements using multicollector (MC)-ICP-MS for the first time.

An advantage of the new TEVA resin column chemis-

try is that the whole column chemistry (from sample loading to Fe collection) finishes <2 hours. Anion exchange resins, AG 1X8 or AG MP-1 employing Fe(III) chloro complex are commonly used [6,7]. In a one milliliter of AG 1X8 column case, for example, the total volume of 55 mL [7], was used from washing the column to collection of Fe. Using an AG MP-1 column, total elution volume for Fe was reduced to 22 mL [6].

For evaluation of column chemistry and mass spectrometry developed in this study, three USGS (the US Geological Survey) standard silicate reference materials, seven GSJ (the Geological Survey of Japan) standard silicate reference materials and three carbonaceous chondrites of Orgueil, Murchison and Allende were used as test samples. Then Fe isotope ratios were measured using a double spike method [8-11] at high mass resolution by MC-ICP-MS to show the validity of the method.

2. Experimental

2.1. Reagents

All experiments were performed in clean rooms and clean benches with HEPA (High Efficiency Particulate

Air) filter in the Pheasant Memorial Laboratory (PML) [12]. Water and HF were purified as described elsewhere [12]. Hydrochloric acid was distilled by a Teflon-two-bottle distiller [12]. TAMAPURE-AA-100 grade perchloric acid (Tama Chemicals Co., Ltd., Japan), electric industry (EL) grade HNO₃ and ultrapure hydrogen peroxide (Kanto Chemical Co. Inc., Japan) were used without purification. Six mol·L⁻¹HCl with 0.05 % (v/v) H₂O₂ was prepared just before the column chemistry. For the column calibration, two multi-element standard solutions (Specpure, Nos. 42885 and 44270, Alfa Aesar, USA) were used.

CAUTION: HF, HCl, HNO₃, HClO₄ and H₂O₂ are highly corrosive and toxic. Inhalation and contact with skin and eyes should be avoided. They should be handled with protective glasses and gloves.

Iron standard metal, IRMM-014 was dissolved, and finally diluted into 1 µg·mL⁻¹ with 0.5 mol·L⁻¹ HNO₃ and used as the isotopic standard for MC-ICP-MS. TEVA extraction resin (100 - 150 µm, Eichrom Technologies, Inc., USA) and Amberchrom CG-71C (Rohm and Haas, Co., USA) were soaked and stored in water. TEVA resin and CG-71C were not reused.

2.2. Iron Double Spike

A ⁵⁷Fe-⁵⁸Fe double spike [10,11] was chosen. Iron isotopes of ⁵⁷Fe and ⁵⁸Fe, with enrichments of 86.06 and 73.51%, respectively, were purchased from Oak Ridge National Laboratory (USA). Each spike was dissolved and diluted with HNO₃, then mixed and used as a Fe double spike. Ideal isotopic abundances of the double spike were 47.65 and 52.35% for ⁵⁷Fe and ⁵⁸Fe, respectively [10], and the best sample: spike mole ratio is 55:45 [10]. Therefore, 1 µg sample Fe was mixed with 0.8 µg double-spike. To keep this ratio, the Fe concentration in the sample solution was determined before the spike addition by high-resolution ICP-MS [13].

2.3. Silicate Samples

Three USGS silicate reference materials, BHVO-1 (basalt), AGV-1 (andesite) and PCC-1 (peridotite) and seven GSJ silicate reference materials, JB-1, JB-2, JB-3 (basalts), JA-1, JA-2, JA-3 (andesites) and JP-1 (peridotite) were used as test samples. Powder of bulk carbonaceous chondrites, Orgueil (C11), Murchison (CM2) and Allende (CV3) were also employed.

2.4. TEVA Resin Column and Silicate Sample Solution

The TEVA resin column was prepared by packing 0.33 mL of TEVA resin on 0.67 mL of CG-71C in a 1 mL polypropylene column (5 cm × 5 mm in diameter, Muro-machi Chemicals Inc., Japan) [4]. The CG-71C resin was

used for absorbing organic materials and controlling the elution rate.

Silicate powder samples were digested by a usual sample digestion method in our laboratory [13]. In short, samples were digested with HF-HClO₄, dried to decompose fluorides with HClO₄ again [14], evaporated with HCl, and finally dissolved with 0.5 mol·L⁻¹ HNO₃. The final dilution was typically ~250 times (20 mg silicate samples into 5 mL).

2.5. Iron Separation by the TEVA Resin Column

A Fe separation procedure using the TEVA resin column is summarized in **Table 1**. All H₂O₂ concentration in **Table 1** is 0.05 % (v/v) H₂O₂. The resin bed was washed twice with 2 mol·L⁻¹ HNO₃, subsequently washed once with 6 mol·L⁻¹HCl, and conditioned. The sample solution containing 1 µg of Fe was added with the solution containing 0.8 µg Fe double spike and 0.6 mL of 6 mol·L⁻¹ HCl, and dried. Then the sample was dissolved with 0.1 mL of 6 mol·L⁻¹ HCl with H₂O₂, loaded on the resin bed and left for 5 min (see Results and Discussion). The major elements were washed away by addition of 3.2 mL of 6 mol·L⁻¹ HCl with H₂O₂. Then Fe was collected with 6.4 mL of 2 mol·L⁻¹ HNO₃. The Fe fraction was dried at 80°C for 10 hours with one drop of HClO₄ to decompose organic materials and small resin particles. To evaporate HClO₄ completely, the sample was finally heated at 195°C for 6 hours. Then the purified Fe was dissolved with 1 mL of 0.5 mol·L⁻¹ HNO₃, which is ready for MC-ICP-MS measurement.

Although the flow rate of the TEVA column is 0.3 mL·min⁻¹, which is rather high, breakthrough of Fe does not occur. As the total elution volume including washing of the column is 32.1 mL, the column chemistry can be finished within two hours including washing and conditioning the resin bed. This is one of the largest advantages of the TEVA resin column chemistry developed in this study. In a case of 1 mL of AG 1X8, the flow rate of a column is ~0.2 mL·min⁻¹, and the total elution volume is ~55 mL [7]. Thus it takes more than 5 hours to collect Fe. In addition in other studies, one pass of anion ex-

Table 1. Chemical procedure for Fe purification using TEVA resin column.

	2 mol·L ⁻¹ HNO ₃	6.4 mL
	water	1.6 mL
Washing	2 mol·L ⁻¹ HNO ₃	6.4 mL
	water	1.6 mL
	6 mol·L ⁻¹ HCl	3.2 mL
Conditioning	6 mol·L ⁻¹ HCl + H ₂ O ₂	3.2 mL
Loading the sample (leave 5 min)	6 mol·L ⁻¹ HCl + H ₂ O ₂	0.1 mL
Removing major elements	6 mol·L ⁻¹ HCl + H ₂ O ₂	3.2 mL
Collecting Fe	2 mol·L ⁻¹ HNO ₃	6.4 mL

change column is not enough, and the column chemistry is repeated twice or three times to purify Fe in some cases [7].

The combination with the double spike technique of this column chemistry gives another advantage that the Fe isotope determination is more tolerable to loss of iron, which could occur in the column chemistry.

2.6. Measurement of Fe Isotope Ratios

Isotope ratios of Fe were measured by an MC-ICP-MS, NEPTUNE housed in PML. Details of the MC-ICP-MS operating conditions are shown in **Table 2**. The spiked $1 \mu\text{g}\cdot\text{mL}^{-1}$ of Fe solution generally gave $\sim 2 \times 10^{-10}$ A signal for $^{56}\text{Fe}^+$, $^{57}\text{Fe}^+$ and $^{58}\text{Fe}^+$. One run consists of 70 scans, but the first 40 scans were not used and the following 30 scans were used, because the signal increased slowly and stabilized after around 40 scans. Thirty sets of isotope ratios of $^{56}\text{Fe}/^{54}\text{Fe}$, $^{57}\text{Fe}/^{54}\text{Fe}$ and $^{58}\text{Fe}/^{54}\text{Fe}$

were obtained for each sample, and the averages of each ratio were calculated. Then the double spike calculation (see the next section) was performed. One T ohm resistor amplifier [15] was used (see **Table 2**), and ^{52}Cr and ^{53}Cr were sometimes observed. Isobaric interference of ^{54}Cr was corrected using $^{54}\text{Cr}/^{52}\text{Cr} = 0.11339$, a power law, and a normalizing value of $^{53}\text{Cr}/^{52}\text{Cr} = 0.028226$ [16]. Nickel interference was corrected using $^{58}\text{Ni}/^{60}\text{Ni} = 2.62$.

The Fe isotope fractionation is expressed as a per mil difference from that of the Fe standard, IRMM-014 [17] by the following equation:

$$\delta^{56}\text{Fe} = \left[\left(\frac{^{56}\text{Fe}/^{54}\text{Fe}}{\text{sample}} \right) / \left(\frac{^{56}\text{Fe}/^{54}\text{Fe}}{\text{IRMM-014}} - 1 \right) \right] \times 1000 \quad (1)$$

2.7. Double Spike Calculation

A theory of a double spike is briefly explained in this section. Each Fe ratio is written using an exponential law as follows:

$$R_{\text{norm-}i/54} / R_{\text{smp-}i/54} = (m_i / m_{54}) \wedge (\phi m_{54}) \quad (2-4)$$

$(i = 56, 57 \text{ and } 58)$

where m_i is a mass of ^iFe ; $R_{\text{norm-}i/54}$ and $R_{\text{smp-}i/54}$ indicate normalizing and sample isotope ratios of $^i\text{Fe}/^{54}\text{Fe}$. In this study, $R_{\text{norm-}i/54}$ ($i = 56, 57$ and 58) are 15.698, 0.36233 and 0.048080, respectively, which are those of the standard IRMM-014 [17]. It should be noted that $R_{\text{norm-}i/54}$ and m_i are constants. ϕ is a mass fractionation factor, which is a product of mass fractionation of the sample and mass discrimination during analysis.

When there is no fractionation in the sample, ϕ is equal to 0. Thus the sample isotope ratios become equal to those of IRMM-014. The purpose is to determine $R_{\text{smp-}i/54}$. For this purpose, a double spike method has been developed [8-11].

The spike isotope ratios of $R_{\text{spike-}i/54}$ ($i = 56, 57$ and 58) also follow the similar equations:

$$R_{\text{spike-}i/54} / R_{\text{spike-}i/54} = (m_i / m_{54}) \wedge (\phi' m_{54}) \quad (5-7)$$

$(i = 56, 57 \text{ and } 58)$

When the spike isotope ratios are measured, only $R_{\text{spike-}i/54}$ are obtained, and $R_{\text{spike-}i/54}$, which are isotope ratios without mass fractionation ($\phi' = 0$), cannot be determined. The method for determination of $R_{\text{spike-}i/54}$, which is called as "spike calibration", is described later.

For the spike-sample mixture, the following equations hold:

$$R_{\text{mix-}i/54} = \left[b(R_{\text{smp-}i/54}) + (R_{\text{spike-}i/54}) \right] / (1+b) \quad (8-10)$$

$(i = 56, 57 \text{ and } 58)$

$$R_{\text{mix-}i/54} / R_{\text{mix-}i/54} = (m_i / m_{54}) \wedge (\phi'' m_{54}) \quad (11-13)$$

$(i = 56, 57 \text{ and } 58)$

Table 2. MC-ICP-MS operating conditions.

1) Sample introduction and ICP conditions						
Nebulizer	Micro-flow PFA nebulizer, PFA-50 (ESI, USA) self-aspiration flow rate: $\sim 50 \mu\text{L}\cdot\text{min}^{-1}$					
Plasma power	1.2 kW (27.12 MHz)					
Torch	Quartz glass torch with a sapphire injector					
Plasma Ar gas flow rate	$15 \text{ L}\cdot\text{min}^{-1}$					
Auxiliary Ar gas flow rate	$0.80 \text{ L}\cdot\text{min}^{-1}$					
Nebulizer Ar gas flow rate	$0.90 \text{ L}\cdot\text{min}^{-1}$					
2) Desolvator conditions						
Desolvator	ARIDUS II					
Spray chamber temperature	110°C					
Desolvator temperature	160°C					
Sweep gas (Ar)	$8 - 9 \text{ L}\cdot\text{min}^{-1}$					
3) Interface						
Sampling cone	Made of Ni					
Skimmer cone	Made of Ni (X-skimmer)					
4) Data acquisition conditions						
Resolution	$M/\Delta M = \sim 7000$					
Washingtime	480 sec after measurement					
Uptake time	90 sec					
Background data integration	4 sec for 1 scan, 20 scans in one run On-top zeroes					
Sample data integration	4 sec for 1 scan, 30 scans in one run					
5) Cup configuration						
L4	L2	L1	C	H1	H2	H4
$^{52}\text{Cr}^*$	$^{53}\text{Cr}^*$	^{54}Fe	^{56}Fe	^{57}Fe	^{58}Fe	^{60}Ni

*An amplifier with a 1 TΩ resistor.

where b is mixing mole ratio of the sample to the spike. The three isotope ratios of the spike-sample mixtures ($R_{\text{mix-}i/54}$; $i = 56, 57$ and 58) are measured. As there are nine variables ($R_{\text{smp-}i/54}$, $R_{\text{mix-}i/54}$, b , ϕ and ϕ'' ; $i = 56, 57$ and 58) and nine equations (Equations (2-4); (8-13)), there should be solutions for these variables. In this study, a calculation [9] to solve these equations was followed, in which exponential approximation is used. Finally, a fractionation degree of the unknown sample, $\delta^{56}\text{Fe}$ (Equation (1)) can be determined.

The spike calibration method is as follows. First, the pure spike is measured. In this study, the averages of the pure spike isotope ratios, $R_{\text{spike-}i/54}$ ($i = 56, 57$ and 58) are obtained to be 25.927, 52.110 and 58.973, respectively. Then, mixtures of the spike and the standard, IRMM-014 were prepared and measured. Then, the spike isotope ratio of $R_{\text{spike-}56/54}$ and ϕ' are determined to minimize the difference between the $^{56}\text{Fe}/^{54}\text{Fe}$ ratio of IRMM-014 and the average of the $^{56}\text{Fe}/^{54}\text{Fe}$ ratio obtained from the double spikes calculation using Microsoft-Excel "Solver".

In the actual sample measurement, the spike-sample mixture is bracketed by the spike-standard mixture. Then from all the spike-standard isotope ratios, the average of $R_{\text{spike-}56/54}$ and the optimum ϕ' in one session are obtained. Then the $^{56}\text{Fe}/^{54}\text{Fe}$ ratios of the sample and the standard before and after the sample measurement are calculated. Finally, $\delta^{56}\text{Fe}$ of each sample is determined. In this calculation, the typical error of $^{56}\text{Fe}/^{54}\text{Fe}$ of the standard solution was 0.06‰ (SD).

3. Results and Discussion

3.1. Kinetic Effects in Adsorption of Fe

For the TEVA resin, kinetic effects in adsorption of Fe are not negligible [5]. Therefore, the kinetic effects in the adsorption of Fe were examined. The Fe standard solutions were loaded on the TEVA column with adsorption time of 5, 10, 25 and 55 min. Then Fe was collected, and the yields were measured.

Analytical results are shown in **Figure 1**. The recovery of Fe was ~100% after 5 min. However, the recovery yields of >5 min seem a bit lower than 100%. Therefore, the optimal adsorption reaction time is determined as 5 min. When the adsorption reaction time becomes longer than 5 min, some Fe ion cannot be desorbed from the resin by 6.4 mL of 2 mol·L⁻¹ HNO₃.

3.2. Elution Curves of Fe in the TEVA Column

An elution curve of Fe of the TEVA column is shown in **Figure 2**. In the figure, only Mg and Fe are plotted, however, other major elements in silicate samples such as Na, Al, P, Ca, Cr, Mn and Ni behave similarly to Mg. As shown in **Figure 2**, almost 100 % of major elements in

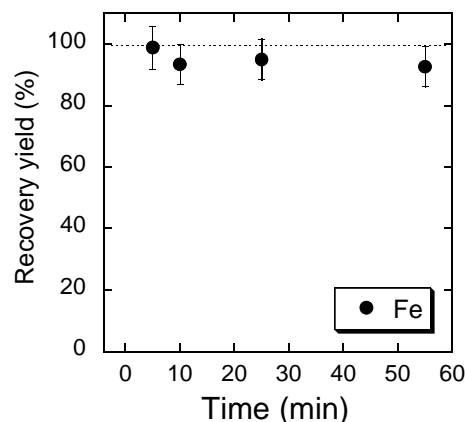


Figure 1. The sample adsorption time (min) after sample loading vs. the recovery yield (%). Error bars are the quantitative analytical error of ~7%. The dotted horizontal line shows 100% yield.

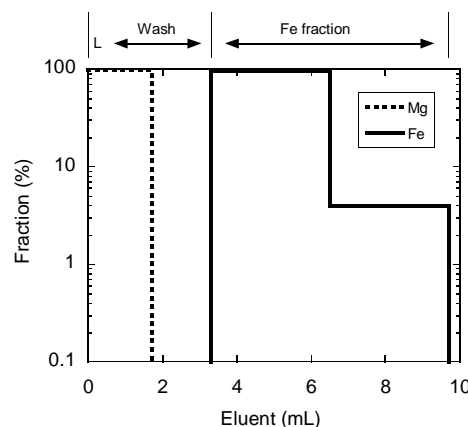


Figure 2. Elution curves of Fe and Mg for the TEVA column. Mg represents behaviors of Na, Al, P, K, Ca, Cr, Mn, Fe, Co and Ni. The horizontal axis shows total eluent volume (mL). The vertical axis indicates fraction (%) recovered from each eluent fraction (%) compared to the added amounts on the column. The vertical axis is in the logarithmic scale. The horizontal arrows at the top show the eluents for wash and Fe fraction, respectively. "L" indicates the sample loading solution.

silicate samples added in the column are washed away in the first 1.6 mL of 6 mol·L⁻¹ HCl with H₂O₂. The total yield of Fe using actual silicate samples was 93.5 ± 6.5 % (SD). This result means that there could be a small loss of Fe in this study. Such loss of Fe could cause isotopic fractionation [18]. However, such fractionation can be corrected by the double spike method employed in this study.

Zinc, Ga, Nb, Mo, Ta, W and U were contained in the Fe fraction with yields of 60% - 90%. However, in usual silicate samples, amounts of these elements compared to 1 µg Fe are <ng levels, therefore, effects of these impurities are inconsequential. Furthermore, total yields of Nb, Ta and W from the sample solution should be lower than

those of the starting solution, because co-precipitation with Ti oxides of Nb, Ta and W should occur during sample evaporation using HClO_4 [19].

The total blanks including sample digestion were 6 ng ($n = 6$). As $\delta^{56}\text{Fe}$ range of all natural samples is $<\pm 3\%$ [7], $\delta^{56}\text{Fe}$ of blank can be assumed to be $<\pm 3\%$. Since Fe in the sample is 1 μg , the maximum shift of $\delta^{56}\text{Fe}$ by the blank should be $<\pm 0.02\%$. As the repeatability of the standard solution was found to be 0.06%, the blank effects are less than one thirds of the repeatability of the standard solution. Thus the blank effect can be neglected.

3.3. Evaluation of Accuracy in Fe Isotope Ratio Measurement

It is difficult to evaluate the accuracy in stable isotope mass spectrometry for less popular elements such as Fe, because the standard materials with accurate isotope ratios are limited. In this study, to examine the accuracy with variable isotope ratios and matrix elements, the synthesized samples were made by mixing of two samples with different isotope ratios and matrix element compositions. Then the isotope ratios of the mixture were compared with the calculated isotope ratios. Such mixing tests were done in studies of Zn and Tl isotopes to evaluate the accuracy of the method [4,20].

For one sample, one of the JB-2 solutions of $\delta^{56}\text{Fe} = -0.27 \pm 0.03$ (see the next section) was used. For the other sample, one of ferruginous bodies-digested solutions [21] of $\delta^{56}\text{Fe} = -3.16 \pm 0.09$ ($n = 4$) (private communication, Makishima and Nakamura, Okayama University, Dec. 2012) was used. This solution was prepared by ashing the ferruginous bodies separated from human lung and dissolving with nitric acid. This solution has a very low $\delta^{56}\text{Fe}$ value, and is mostly composed of Fe [21]. The JB-2 and ferruginous bodies-digested solutions were taken and mixed to contain 1 μg of Fe. Three types of the mixtures with different matrix compositions were made. For each type of the mixtures, four or five samples were made. Each sample was added with 0.4 mL $6 \text{ mol}\cdot\text{L}^{-1}$ HCl and the Fe double spike, dried and passed through the TEVA column. Then Fe was collected and its isotope ratio was determined by MC-ICP-MS.

Analytical results of the $\delta^{56}\text{Fe}$ value of each mixture are shown in **Table 3**. The calculated values are also shown in **Table 3**. The error in calculation for each mixture was based on concentration error of $\sim 5\%$ of two

starting solutions, and no other errors are taken into account. From **Table 3**, the observed values are consistent with the calculated values within 2SD ranges, although the three samples had different major element compositions. Therefore, it is suggested that the double spike method for Fe isotope measurements using MC-ICP-MS in this study gives accurate isotope ratios of Fe.

3.4. Fe Isotope Ratio Measurements in Silicate Reference Materials

The TEVA column chemistry developed in this study was applied to analysis of the silicate reference materials, and analytical results are presented in **Table 4**, together with the reported values [11,22-26]. To make the comparison between $\delta^{56}\text{Fe}$ of this study and those of references easier, they are plotted in **Figure 3**. The $\delta^{56}\text{Fe}$ value of BHVO-1 in this study of 0.18‰ is a little higher than those of references [22-24,26]. The $\delta^{56}\text{Fe}$ values of AGV-1 and PCC-1 of this study are -0.10 and 0.00% , respectively, which are consistent with those of previous studies [21,25,26] when errors are taken into account.

Repeatability for silicate reference materials (**Table 4**) is 0.03% - 0.06%, and the average is 0.05%. This 0.05% should be considered as repeatability of actual silicate analysis by MC-ICP-MS in this study. As discussed previously, the blank effects are $\pm 0.02\%$, however, this can be negligible to 0.05%, which is considered to be repeatability of this method. This value is similar to that of the pure standard solution (0.06%).

The repeatability in the Fe standard solution is compared with those of references here. The SD values of replicate analyses of the standard solution are 0.013, 0.10, 0.010, 0.050 and 0.041‰ in Chicago [22], Woods Hole [23], Hannover [24], Madison [25], and Frankfurt [26] groups, respectively. Therefore the repeatability of the MC-ICP-MS methods of these leading groups which use the bracketing method is similar or a bit better than that of this study. However, all groups use AG 1X8, so they need repetitive column chemistry in many cases, because Fe cannot be purified enough by the single column chemistry to be used in the mass spectrometry. However, other groups [11] which use AG MP-1 can purify Fe by a single column chemistry.

Recently, Millet *et al.* [11] achieved "ultra-precise" Fe measurements, using the same pair of the double spike, ^{57}Fe - ^{58}Fe . They constantly achieved the repeatability of

Table 3. Analytical results of mixing experiments.

	Calculated		Observed		
	$\delta^{56}\text{Fe}$	SD (%)	$\delta^{56}\text{Fe}$	SD (%)	n
Mixture#1	-1.12	0.08	-1.36	0.04	4
Mixture#2	-1.90	0.13	-2.00	0.19	4
Mixture#3	-2.50	0.17	-2.64	0.05	5

Table 4. $\delta^{56}\text{Fe}$ values of USGS and GSJ silicate reference materials and carbonaceous chondrites.

Sample	Average $\delta^{56}\text{Fe}$	SD (%)	n	References (Error is SD)
BHVO-1	0.18	0.03	3	0.105 ± 0.008 [22], 0.110 ± 0.060 [23], 0.109 ± 0.024 [24], 0.117 ± 0.015 [26]
AGV-1	-0.10	0.06	3	0.04 ± 0.01 [24]
PCC-1	0.00	0.02	3	0.025 ± 0.012 [22], -0.06 ± 0.06 [25], 0.043 ± 0.013 [26]
JB-1	-0.14	0.05	4	
JB-2	-0.27	0.03	4	0.073 ± 0.014 [11]
JB-3	-0.35	0.08	3	
JA-1	-0.13	0.06	4	0.060 ± 0.010 [11]
JA-2	-0.02	0.03	4	
JA-3	0.09	0.06	4	
JP-1	-0.54	0.06	4	
Orgueil	-0.05	0.06	3	-0.015 ± 0.074 [26], 0.38 [27], 0.04 ± 0.06 [28]
Murchison	-0.10	0.12	3	-0.12 ± 0.06 [28]
Allende	-0.03	0.03	3	-0.007 ± 0.012 [22], -0.04 [27], -0.06 ± 0.01 [28]

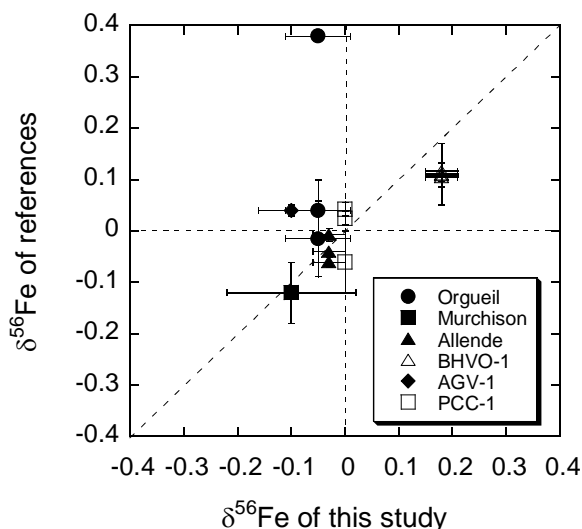


Figure 3. Iron isotope ratios ($\delta^{56}\text{Fe}$) of this study vs. those of references. The error bars show one standard deviation of repeatability (SD, %). The vertical and horizontal dotted lines show $\delta^{56}\text{Fe} = 0$ of this study and references, respectively. The dotted slope line indicates slope = 1, which means that there is no difference in $\delta^{56}\text{Fe}$ between this study and references.

0.01‰ using double-spike-MC-ICP-MS. The largest difference of this study from their study is 1) enrichment of the double spike and 2) larger usage of the sample. The $^{56}\text{Fe}/^{54}\text{Fe}$, $^{57}\text{Fe}/^{54}\text{Fe}$ and $^{58}\text{Fe}/^{54}\text{Fe}$ ratios of the spike in this study are 24.5521, 53.0182 and 48.0436, while those of their spike are 2031, 67300 and 6812, respectively. This means that the denominator isotope, ^{54}Fe of this study is far more abundant than that of Millet *et al.* [11], resulting in lower precision. In addition, Millet *et al.* [11] used a $100 \mu\text{L}\cdot\text{min}^{-1}$ nebulizer and $2 \mu\text{g}\cdot\text{mL}^{-1}$ solution, totally 4 times larger amounts of Fe are used than that in this study.

3.5. Application to Measurements of $\delta^{56}\text{Fe}$ in Carbonaceous Chondrites

The $\delta^{56}\text{Fe}$ values of carbonaceous chondrites, Orgueil, Murchison and Allende were measured by the method developed in this study. The $\delta^{56}\text{Fe}$ value of Orgueil of this study agrees well with those of Weyer *et al.* [26] and Kehm *et al.* [28], but that of Zhu *et al.* [27] seems a bit higher. The $\delta^{56}\text{Fe}$ values of Allende of this study also agrees well with those of previous studies [22,27,28]. However, numbers of analyses of carbonaceous chondrites in literatures are limited, and carbonaceous chondrites could be heterogeneous, thus further studies are required.

Interference ratios of $^{54}\text{Cr}/^{54}\text{Fe}$ and $^{58}\text{Ni}/^{58}\text{Fe}$ in these carbonaceous chondrite analyses after the column chemistry were $<1.6 \times 10^{-3}$ and $<1.4 \times 10^{-4}$, respectively. Large Cr and Ni corrections were needed in the TEVA column chemistry developed in this study, however, the analytical results suggest that the single-pass TEVA column is sufficient even in analyses of Cr rich samples such as peridotites ($\sim 3000 \mu\text{g}\cdot\text{g}^{-1}$) or chondrites ($\sim 4000 \mu\text{g}\cdot\text{g}^{-1}$).

4. Conclusions

Using an extraction resin, TEVA, new column chemistry for separating Fe has been developed for Fe isotope ratio determination by MC-ICP-MS. Iron was purified by $6 \text{ mol}\cdot\text{L}^{-1}$ HCl + H_2O_2 , and major elements were separated. Fe was finally recovered with $2 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 . The recovery yields and total blanks were $93.5\% \pm 6.5\%$ (SD) and 6 ng, respectively.

For evaluation of the separation method, Fe isotope ratios were measured by a double spike method using MC-ICP-MS, respectively. Repeatability obtained from actual analyses of USGS standard reference materials of

BHVO-1, AGV-1, PCC-1, and GSJ standard silicate materials of JB-1, JB-2, JB-3, JA-1, JA-2 and JA-3 were 0.05‰ (SD). Fe isotope ratios of carbonaceous chondrites of Orgueil, Murchison and Allende were also determined by the column chemistries developed in this study.

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