Tin isotope analysis of cassiterites from Southeastern and Eastern Asia

ERIKA YAMAZAKI,[1,2] SHUN'ICH NAKAI,[2]* TETSUYA YOKOYAMA,[1] SHUNSO ISHIHARA[3] and HONGFENG TANG[4]

[1]Department of Earth and Planetary Sciences, Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8851, Japan
[2]Earthquake Research Institute, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-0032, Japan
[3]Geological Survey of Japan, AIST, Tsukuba, Ibaraki 305-8567, Japan
[4]Laboratory for Study of the Earth's Interior and Geofluids, Institute of Geochemistry, CAS, Guiyang 550002, China

An analytical technique is presented for isotope analysis of a Sn ore mineral, cassiterite. Hydroiodic acid was used to successfully decompose the cassiterite samples. An extraction chromatographic material, TRU resin was utilized for the chemical purification of Sn. Although it has been confirmed that this purification process causes isotopic fractionation, the effect can be corrected. The purification method was used to investigate natural isotopic variations in Sn in cassiterite from Asian countries (Japan, China, Thailand, and Malaysia), via multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS).

Consequently, isotopic variations as large as 0.77‰ in $^{124}Sn/^{120}Sn$ were observed for cassiterite samples from Japan and China. The isotopic fractionations of all the samples were dependent on isotope mass. However, the cause of Sn isotopic variation is yet to be established.

INTRODUCTION

Tin has ten stable isotopes, with the isotope mass varying from 112 to 124. This is the largest number of stable isotopes among all elements of the periodic table, rendering Sn a unique element. The heavier isotopes of Sn were synthesized in the universe by the rapid and slow neutron capture processes (r- and s-process), whereas lighter isotopes were produced by a proton capture or photo dissociation reaction (p-process) (e.g., Burbidge *et al.*, 1957). Based on their cosmochemical interest, nucleosynthetic Sn isotope anomalies in meteorites have been investigated since the 1960s. De Laeter and Jeffery (1965), however, found no significant isotope anomalies in meteorites. Although Loss *et al.* (1990) observed small excesses of minor Sn isotopes in acid-etched residues, the discrepancy was attributed to analytical problems. At the same time, the variation in natural Sn isotope compositions in terrestrial samples has been of great interest to geochemists (De Laeter and Jeffery, 1965, 1967; Rosman and McNaughton, 1987; McNaughton and Loss, 1990; McNaughton and Rosman, 1991; Clayton *et al.*, 2002; Haustein *et al.*, 2010). Among these studies, Haustein *et al.* (2010) reported the largest Sn isotopic variation

(0.55‰ per unit mass difference) in cassiterite, a terrestrial Sn mineral. Cassiterite is a well-known major ore mineral for Sn, and has been widely used as a raw material for Sn metal and bronze alloys since ancient times. If there are significant isotopic variations between different ores, the Sn isotopic ratio may be used for provenance studies, similar to the well-studied Pb isotopes. Therefore, the variation in natural Sn isotopes is also an important research target for archaeology (Budd *et al.*, 1995; Haustein *et al.*, 2010; Nickel *et al.*, 2011).

In pioneering studies, Sn isotopes were studied by thermal ionization mass spectrometry (TIMS) (De Laeter and Jeffery, 1965, 1967; Devillers *et al.*, 1983; Rosman *et al.*, 1984; Rosman and McNaughton, 1987; Loss *et al.*, 1990; McNaughton and Loss, 1990; McNaughton and Rosman, 1991; Gale, 1997). However, the relatively high ionization potential of Sn (7.3 eV) hindered Sn ionization by TIMS, which made high-precision isotope analysis difficult. In contrast, plasma-source mass spectrometry enables relatively higher ionization for most elements in the periodic table, including those with high ionization potential. Thus, following the development of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS), Sn isotope analyses have been performed mainly by this method (Lee and Halliday, 1995; Clayton *et al.*, 2002; Moynier *et al.*, 2009; Osawa *et al.*, 2009; Haustein *et al.*, 2010; Nickel *et al.*, 2011).

This study focused on the development of Sn isotope

---

*Corresponding author (e-mail: snakai@eri.u-tokyo.ac.jp)

analysis for cassiterite samples by using MC-ICP-MS, with a view to future applications of Sn isotopes within archaeology. Although Haustein *et al.* (2010) detected Sn isotopic variations in cassiterites, there is limited data on Sn isotope compositions in natural samples. This partly resulted from the resistance of cassiterite to acid attack, commonly used for chemical decomposition of minerals. Furthermore, the solution containing Sn requires careful handling because Sn is readily oxidized and precipitates in concentrated nitric acid as metastannic acid (Kragten, 1975). Although Sn is treated with hydrochloric acid, careful handling is required when evaporating the solution because stannic chloride ($SnCl_4$) vaporizes at 114°C (e.g., Lide, 1993–1994), which could cause loss of Sn. Thus far, alkali fusion techniques (Hall, 1980; Sear, 1997) and the reduction of Sn by graphite (Hall, 1980; Clayton *et al.*, 2002) were used for decomposing the minerals. These methods are conducted under an open environment and require a high temperature of about 1200°C, which may cause loss of volatile tin. Haustein *et al.* (2010) applied potassium cyanide reduction to Sn from cassiterites. Their decomposition technique required a temperature of around 800°C, which is lower than that used in previous methods; however, potassium cyanide is very poisonous and difficult to handle. In contrast, a classical study by Caley (1932) successfully decomposed cassiterites with hydroiodic acid (HI) at a relatively low temperature (100°C).

In this study, we present a technique for decomposing cassiterites with HI and a subsequent chemical separation technique for Sn, using an extraction chromatographic resin. We also quantitatively evaluate possible Sn isotope fractionation during the purification process. The accuracy of Sn isotope analysis using MC-ICP-MS including chemical purification processes is discussed. Finally, we present Sn isotope compositions in cassiterites from Southeast and Eastern Asia, including Japan.

EXPERIMENTAL METHOD

Materials and reagents

High-purity water (18.3 MΩ·cm) from a Milli-Q system (Millipore Corp.) was used. Hydroiodic acid (Kanto Chemical Co., Inc., #18086-30) was used for the decomposition of cassiterite. Ultrapure-grade HNO_3, HCl, HF, and $HClO_4$ (Kanto Chemical Co., Inc., #18078-1B, #28163-1B, 18083-1B, and 32059-1B, respectively) were used without purification for sample decomposition and other analytical procedures. PFA vials (volume: 3 mL, Savillex 0023R) were used to decompose cassiterite samples. Cassiterite sample solutions dissolved in HI were stored in high-density polyethylene (HDPE) bottles (NALGENE) because HI corrodes low-density polyethylene bottles (LDPE). Other sample solutions were stored in LDPE bottles (NALGENE). An extraction chromatographic resin (TRU Resin; particle size: 100–150 μm, Eichrom Technologies, Inc., #TRU-B50-A) was used for Sn purification. A polypropylene column (Muromac column M; resin bed size: 1 mL, Muromachi Technos Co., Ltd., Japan) was used for the column chemistry.

Standard solutions

Three commercial Sn solutions were used for isotope and concentration standards. An in-house standard for isotope analysis was prepared from a Sn standard solution dissolved in 1% HNO_3 and 1% HF, provided by SPEX CertiPrep (CLSN2-2Y, Lot#CL5-45SN, hereafter referred to as "SPEX1"). In this study, all Sn isotope data measured by MC-ICP-MS are reported in δ notation against this standard (see below). Another Sn standard solution from SPEX, dissolved in 20% HCl media (PLSN5-2Y, Lot#14-84SN, hereafter referred to as "SPEX2"), was used to evaluate potential isotopic fractionation during the purification process and to confirm the reproducibility of analytical procedures. We also used the standard reference material 3161a (Lot#070330) provided by the National Institute of Standards and Technologies (NIST) to examine the long-term reproducibility of isotope measurement. In addition, a Sb standard solution (Cat#PLSB7-2Y, Lot#13-134SB; SPEX CertiPrep) was used to correct for mass biases in Sn isotope analysis using MC-ICP-MS (Clayton *et al.*, 2002).

In order to evaluate the recovery yield and purity of Sn through sample decomposition and purification processes, a mixed standard solution containing 50 elements (hereafter referred to as "MIX50") was prepared from six single-element standard solutions (Sn: SPEX2; Cu, Cd: Wako Pure Chemical Industries, Ltd.; Sb, Te, Pb: Kanto Chemical Co., Inc.) and two multi-element standard solutions, XSTC-8 and XSTC-13 (SPEX CertiPrep). XSTC-8 contains 13 elements (B, C, Ge, Mo, Nb, P, Re, S, Si, Ta, Ti, W, Zr) and XSTC-13 contains 31 elements (Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Hg, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Th, Tl, U, V, Zn).

As described above, we used two Sn standard solutions obtained from SPEX: SPEX1 dissolved in HNO_3 and HF, and SPEX2 dissolved in HCl media. It was reported that the presence of HCl in a Sn-containing solution could shift the signal intensities of Sn in ICP-MS analysis (Saeki *et al.*, 1998), possibly leading to an isotopic shift. Thus, SPEX1 without HCl was used as an in-house standard in MC-ICP-MS analysis. In contrast, SPEX2 was used to evaluate the performance of column chemistry using TRU resin, in which the sample solution was first introduced into the column as 0.5M HCl. SPEX1, dissolved in HNO_3 and HF, was not used for this purpose because conversion to the chloride form requires evapo-

Table 1. Cassiterite samples from Asian countries

Sample	Locality	Type of the deposit	Mineralization age	Sediment rocks age
Japan				
KN1979	Kaneuchi mine, Kyoto	pegmatitic or plutonic vein [1,2]	91 Ma (muscovite) [3]	Paleozoic [1,2]
M21406	Ohtani mine, Kyoto	W–Sn–Cu vein [1]	93 Ma (biotite), 90-91Ma (muscovite) [3]	Paleozoic [1]
M21797	Kiwada mine, Yamaguchi	skarn and quartz vein [4]	96 Ma (muscovite) [3]	Paleozoic [4]
M22550	Ikuno mine, Hyogo	xenothermal deposit [5]	63–74 Ma (adularia) [7]	Permian [6]
M22561	Takatori mine, Ibaraki	W–Cu–Sn plutonic vein [8]	69 Ma (muscovite) [3]	Triassic [8]
M. Kano	Kano mine, Miyazaki	contact type and high-T vein [9]	Miocene* [9]	Paleozoic [10]
M22545	Naegi district, Gifu	vein or pegmatite? [11]	64–68 Ma (biotite) [12], 67 Ma (monazite) [13]	Jurassic [14]
China				
HY38	Sareshke deposit, East Junggar, Xinjiang	cassiterite–quartz vein [15]	307 Ma (molybdenite) [15,16]	Devonian to Carboniferous [15]
GL1	Ganliangzi deposit, East Junggar, Xinjiang	greisen type [17]	315 Ma (muscovite) [17], 305 Ma (fluid inclusion) [18]	—
KM3	Kamst deposit, East Junggar, Xinjiang	greisen type [17]	307 Ma (muscovite) [17]	—
KM08-1	Kamst deposit, East Junggar, Xinjiang	The same as above.	The same as above.	The same as above.
Gejiu	Gejiu, Yunan	stratiform sulphide/skarn sulphide/vein type [19]	80–240 Ma [20,21]	Triassic [20,22]
Dulong	Dulong, Yunan	Sn–Zn cassiterite–sulphide deposit [22,23]	80–190 Ma [24]	middle Cambrian [22,23]
YB-17	Yanbei, Jiangxi	porphyry Sn deposit [25,26]	114 Ma (whole rock) [27], 126, 128 Ma (fluid inclusion) [28]	Mesozoic [25,26]
Thailand				
Yod Nam	Yod Nam mine, Suba Drive	greisen type Sn–W deposit [29]	68 Ma (muscovite), 81 Ma (whole rock) [29]	Paleozoic and Triassic [29]
77120503-2	Kosaba mine	low-T exogranitic deposit [29]	—	Paleozoic [29,30]
77120503-3	The same as above.	The same as above.	The same as above.	The same as above.
Malaysia				
780326-5	Kinta Valley	placer [30]	Triassic (207–230 Ma) [30] [1,2]	Palaeozoic [30]

1) Imai et al. (1972), 2) Haraguchi and Kikuchi (1952), 3) Shibata and Ishihara (1974), 4) Nagahara (1978), 5) Park and MacDiarmid (1964), 6) Tanaka et al. (1971), 7) Ministry of International Trade and Industry of Japan (1987), 8) Ikeda et al. (1983), 9) Council of Underground Resources Development (1956), 10) Adachi (1997), 11) Shibata et al. (1939), 12) Shibata et al. (1962), 13) Suzuki et al. (1994), 14) Ishihara and Wu (2001), 15) Su et al. (2007), 16) Tang et al. (2009), 18) Chen et al. (1999), 19) Zhang et al. (2007), 20) Wang (1983), 21) Qin et al. (2006), 22) Chen et al. (1992), 23) Li (1988), 24) Xu and Zhu (1988), 25) Xiong et al. (1994), 26) Shen et al. (1996), 27) Shen and Ling (1994), 28) Mei et al. (2007), 29) Ishihara et al. (1980), 30) Cobbing et al. (1992), 31) Bignell and Snelling (1977), 32) Liw and Page (1985).
*Estimation for Mitate mine, which is adjacent to Kano mine.

Table 2. Procedure for separation of Sn (modified from Yi et al., 1995)

Operation	Solvents	
Washing	5 mL of 0.5 M HCl, 5 mL of Milli-Q	2 cycles
Conditioning	4 mL of 0.5 M HCl	
Loading	2 mL of 0.5 M HCl	
Elution 1	3 mL of 0.5 M HCl	
Elution 2	20 mL of 0.25 M HCl	
Elution 3	16 mL of 0.4 M HNO_3	
Add	0.285 mL of 0.1 M HF	

Table 3. Operating parameters for Sn isotope analysis

Operating parameters	
MC-ICP-MS	IsoProbe
RF Power (W)	1350
Acceleration voltage (V)	5990–6020
Coolant Ar flow (L min^{-1})	14
Intermediate Ar flow (L min^{-1})	1
Nebulizer Ar flow (L min^{-1})	0.9–1.0
Desolvator	Aridus
Ar sweep gas flow (L min^{-1})	3.3–3.6
N2 gas flow (L min^{-1})	0.02
Solution uptake rate (μL min^{-1})	60
Spray chamber temperature (°C)	95
Desolvator temperature (°C)	160
Analytical parameters	
Cycles per block	100
Number of blocks	1
Sample rejection (%)	5
Integration time (s)	5

ration of acids, which may cause Sn isotope fractionation via Sn oxidation. It is important to note that Sn isotopic compositions for SPEX1 and SPEX2 are not necessarily identical to each other.

Cassiterite samples and decomposition procedure

Cassiterite (SnO_2) is a primary ore of Sn. In this study, we analyzed cassiterite samples from Southeast- and East Asian countries: Japan, China, Thailand, and Malaysia. Sample locality, type of deposit, mineralization age, and host rock age are summarized in Table 1.

Cassiterite samples were crushed in a stainless steel mortar and powdered in an agate mortar. About 1 mg of powdered sample was weighed in a 3-mL PFA vial, and 0.3 mL of HI was added for sample decomposition (Caley, 1932). The vial was tightly capped, and put in an A255AC Teflon liner of a Teflon-lined digestion bomb (Parr 4745). About 1 mL of Milli-Q water was added in the Teflon liner to balance the internal pressure of the PFA vial and the Teflon liner. The Teflon-bomb was heated in an oven for 24 h at 100°C. Subsequently, the sample was dried at ~80°C and leached with 0.6 mL of HCl. The supernatant solution was collected in an HDPE bottle. The procedure was repeated until the sample was completely dissolved or repeated up to four times. In some cases, white precipitates remained in the vial, which are most likely silicate minerals. Although we attempted to entirely decompose these residues by means of HF, $HClO_4$, and HNO_3, the residues remained. Therefore, they are most likely insoluble silicates, which require Teflon-bomb digestion at a higher temperature (>200°C). In this study, we analyzed Sn isotope compositions in the HI dissolved fractions. Sn blank for this decomposition process was around 1 ng.

Purification of Sn

In Sn isotope analysis using MC-ICP-MS, Cd, In, Te, and Xe are potential isobaric interferences. In addition, any coexisting elements at relatively high concentrations in the analyzing solution would cause matrix-derived isotopic fractionation of Sn, which can result in erroneous data. Ion-exchange chromatography was commonly used to purify Sn from other elements (De Laeter and Jeffery, 1965, 1967; De Laeter *et al*., 1974; McNaughton and Rosman, 1991). Recently, an extraction chromatographic material, TRU resin (Eichrom Industries Inc.), has become popular for Sn purification because of its simplicity and high recovery yield (Yi *et al*., 1995; Haustein *et al*., 2010; Nickel *et al*., 2011). In this study, we modified the previous purification methods using TRU resin as follows.

To pre-clean the TRU resin, it was put into a Teflon vial with 2% HNO_3 and was heated at 50°C for 4–5 h. Then, the resin floated and was removed using a pipette. Subsequently, 2% HNO_3 was added to the vial, and this procedure was repeated three times. Finally, the TRU resin was stored in 2% HNO_3. Then, 1 mL of the TRU resin was charged in a polypropylene column. The detailed procedure to separate Sn is presented in Table 2. At the end of the separation process, we collected Sn in 16 mL of 0.4 M HNO_3 solution, immediately followed by the addition of 0.285 mL of 0.1 M HF to the Sn fraction in order to prevent Sn precipitation (Yi *et al*., 1995). Sn blank for the purification process was around 10 ng. The recovery and isotopic fractionation of Sn during the separation procedure were examined using the mixed standard solution containing 50 elements (MIX50) described above. The prepared test solution contained 1.5 μg/mL of Sn, 7.5 μg/mL of Cu, 0.75 μg/mL of Pb, and 0.3 μg/mL for the rest of the elements. The composition of the test solution simulates that of bronze solutions, with a view to future applications involving archaeological samples.
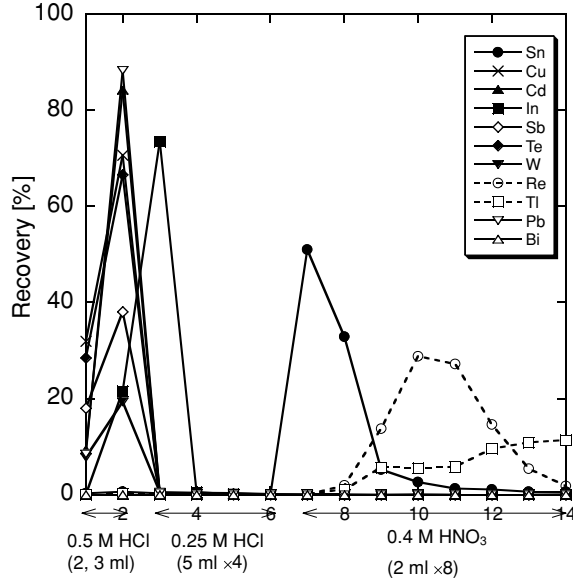
Fig. 1. Separation of Sn by TRU resin.

Fig. 2. Long-term variation in Sn isotope ratios for NIST SRM 3161a. Open symbol is δ-value in one day, and closed circle is average of all measurements. Uncertainty is 2SE for each measurement, and 2SD for the average.

Tin isotope measurements by MC-ICP-MS

Tin isotopic ratio measurements were carried out using a MC-ICP-MS (IsoProbe, Micromass) equipped with nine Faraday cups, installed at the Earthquake Research Institute, University of Tokyo. The instrument is composed of a standard ICP source and magnetic mass analyzer with an ion transfer system based on an RF-only hexapole cell. Sample solutions were introduced into the ICP through a desolvation system, ARIDUS (CETAC Co.). We monitored seven isotopes (114, 116, 117, 118, 120, 122, and 124) for Sn and two isotopes (121, 123) for Sb. Ion currents of these isotopes were simultaneously collected by L3-H6 Faraday cups. Isotopes of ^{112}Sn, ^{115}Sn, and ^{119}Sn were not monitored because the number of collectors is limited. A single isotope run consists of 100 measurements of 5 s integration in each scan. Detailed operating parameters are shown in Table 3. All sample solutions were diluted to Sn = 60 ppb with 2% HNO$_3$ containing trace amount of HF. For 60 ppb solutions, we obtained total Sn signals of ~14 × 10^{-11} A. The hydride formation rate estimated from a signal at mass of 125 and that of ^{124}Sn was less than 6 × 10^{-6}. We also added a standard solution of Sb for mass bias correction (Clayton *et al.*, 2002) such that the Sb concentration was 30 ppb.

Mass fractionation correction during isotope analysis was carried out by combining the external correction method and standard bracketing method. In this study, we applied the exponential law (Russell *et al.*, 1978) using the following equation:
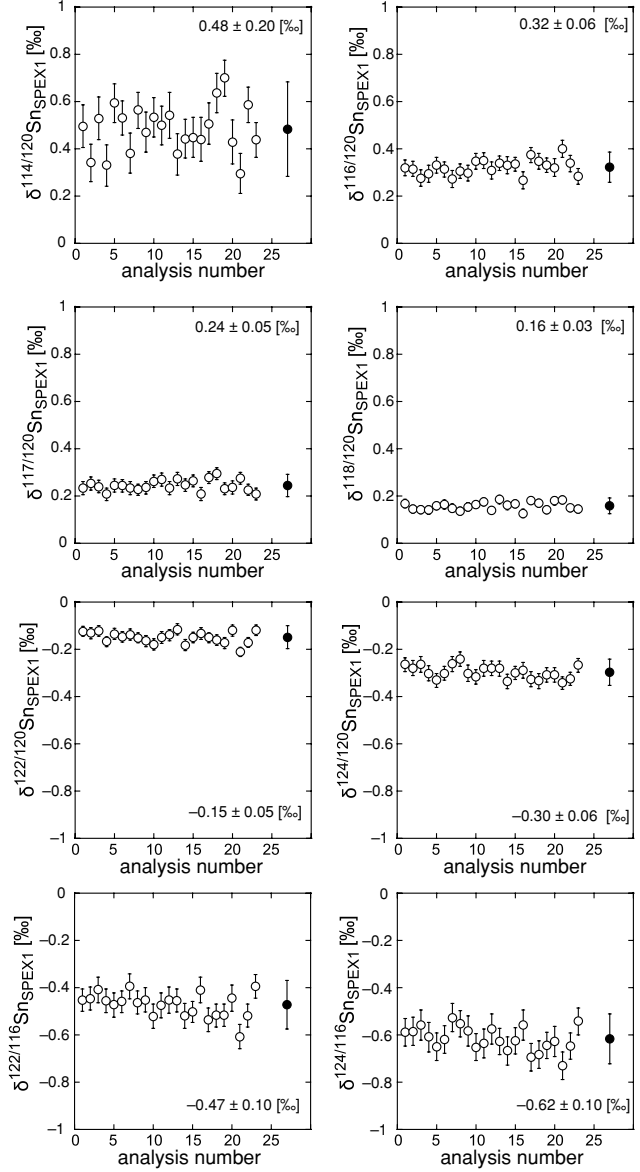
$$r_i = R_i \left(\frac{M_i}{M_k} \right)^{\beta} \qquad (1)$$

where M_i and M_k are the masses of the target isotopes and the reference isotope, respectively, and r_i and R_i represent the fractionation-corrected isotopic ratio and observed isotopic ratio for the element of interest, respectively. The mass bias factor, β, can be estimated from the following equation:

Tin isotope analysis of cassiterites   25

Table 4. Tin isotopic fractionation during the purification process

		[‰]	$\delta^{124/120}$Sn	2SE	2SD
Mix standard		1	–0.71	0.03	
(Sn + other elements)		2	–0.64	0.04	
		3	–0.64	0.03	
		Average	–0.67		0.08
Only Sn (SPEX2)	Batch 1	1	–0.63	0.03	
		2	–0.62	0.03	
		3	–0.64	0.03	
		Average	–0.63		0.02
	Batch 2	1	–0.69	0.03	
		2	–0.61	0.03	
		3	–0.64	0.03	
		Average	–0.65		0.08
	Batch 3	1	–0.75	0.03	
		2	–0.68	0.03	
		3	–0.72	0.03	
		Average	–0.72		0.07
	Batch 4	1	–0.64	0.03	
		2	–0.68	0.02	
		3	–0.71	0.03	
		Average	–0.68		0.07
	Batch 5	1	–0.61	0.03	
		2	–0.60	0.03	
		3	–0.59	0.03	
		Average	–0.60		0.01
	Only Sn average		–0.65		0.09
Total average			–0.66		0.09

$$\beta = \frac{\ln\left(r_i^{ext}/R_i^{ext}\right)}{\ln\left(M_i^{ext}/M_k^{ext}\right)} \qquad (2)$$

where M_i^{ext} and M_k^{ext} are the masses of an externally doped element and r_i^{ext} and R_i^{ext} represent the true and observed isotopic ratios for the doped element, respectively. The external standardization method was originally proposed by Longerich *et al.* (1987) for Pb isotope measurement, and it was extended to other elements. This correction assumes that the mass fractionation factor is equal between the target element and doped element (in our case, Sn and Sb, respectively). Because there is no Sb reference material with certified isotopic composition, we accepted ^{123}Sb/^{121}Sb = 0.7479 (De Laeter *et al.*, 2003) as being the true isotopic ratio.

We also used the standard-sample bracketing method to correct for the mass discrimination effect during MC-ICP-MS analysis, in which a standard solution was measured before and after sample measurement. In this study,

the corrected isotope ratios of a sample are expressed in δ notation as deviations from those of SPEX1, calculated by the following equation:

$$\delta_{i_{SPEX1}} = \frac{r_i^{smp} - r_i^{SPEX1}}{r_i^{SPEX1}} \times 10^3 \qquad (3)$$

where r_i^{SPEX1} is the mean isotopic ratio of SPEX1 measured before and after the target sample.

RESULTS AND DISCUSSION

Performance of Sn purification

Figure 1 shows the elution profile of the Sn separation procedure with TRU resin, using the mixed standard solution (MIX50) as a starting material. TRU is an extraction chromatographic resin in which the extractant system is octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO) dissolved in tri-*n*-butyl phosphate (Horwitz *et al.*, 1993). The resin has large
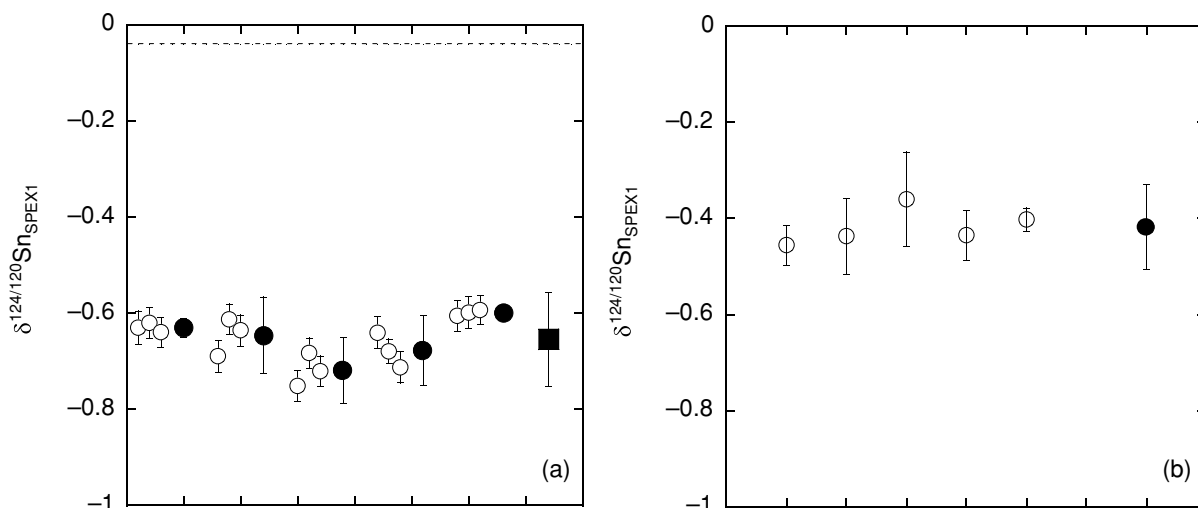
Fig. 3. (a) Repeated analysis for purified Sn standard solutions. Open circles are each measurement, closed circles indicate the average of each batch analysis, and closed square is total average. Uncertainties are 2SE for each measurement, and 2SD for average values. (b) Repeated analysis of the purified cassiterite sample (Naegi district, Japan). Isotopic measurements were carried out three times for each. Uncertainties are 2SD. Open circle represents each δ-value of the batches, and closed circle indicates the average of five batches. These δ-values are not corrected for the modification of isotopic ratios in the purification process.

partition coefficients for some actinides (e.g., Th, U, Np, Pu) as well as Sn in HCl media, whereas the affinity of Sn to this resin decreases in HNO_3 media. Thus, most of the unwanted elements—including Cd, In, and Te—that can interfere with Sn isotope analysis appear within the first (0.5 M HCl) or second (0.25 M HCl) fraction. Tin is collected by 16 mL of 0.4 M HNO_3 together with Re and Tl, which would not interfere with the Sn isotope analysis. The recovery of Sn was 95.3 ± 1.6%. Minor signals of Cd, In, Sb, and Te were sometimes found in the purified Sn fraction. However, concentrations of the impurity were less than one-thousandth that of Sn, and those impurities caused no influence on observed Sn isotope ratios except for minor Sn isotopes such as [114]Sn. The total blank for Sn was around 10 ng. Because we used 1500 ng of tin for each sample preparation and the difference in isotope compositions between the sample and blank is small, it is not likely that the blank caused isotope shift.

Haustein *et al.* (2010) also used TRU resin for Sn separation, although they employed a slightly different procedure from Yi *et al.* (1995) and the present study. After conditioning the resin with 5 mL of 1 M HCl, they loaded the sample solution dissolved in 10 mL of 1 M HCl, followed by 10 mL of 1 M HCl and 6 mL of 5 M HNO_3. Then, they recovered Sn with 4 mL of 1 M HNO_3. We attempted to reproduce this procedure; however, Sn was completely eluted in the 5 M HNO_3 fraction. The inconsistency may have resulted from a variation in the chemi-

cal form of Sn in the loading solution, such as the oxidation state of Sn. Tin in the MIX50 used in this study was prepared from the SPEX2 solution, of which the solvent is HCl media. Because SPEX2 was prepared by dissolving Sn metal in HCl (personal communication from SPEX CertiPrep), it is likely that Sn is present as Sn^{2+} in the solution. The other elements in MIX50 were prepared from multiple solutions, some of which were dissolved in diluted HNO_3. However, they were evaporated to remove HNO_3 before mixing, to prevent the oxidization of Sn. Thus, it is likely that Sn oxidation states in both studies are the same. At present, the reason for the different elution profiles is not clear, and we conclude that it is safe not to use 5 M HNO_3 in the column chemistry before collecting Sn. The results of tests to evaluate Sn isotope shift during separation column separation will be described in the later section, titled "Evaluation of Sn isotope shift in column chemistry."

Long-term reproducibility of SRM 3161a analysis by MC-ICP-MS

We repeatedly analyzed the Sn standard solution (NIST SRM 3161a) to evaluate the long-term (around two months) reproducibility of isotope measurements using MC-ICP-MS. The Sn concentration in the standard solution was fixed at 60 ppb, and Sb was mixed to be 30 ppb for the external standardization. Previous studies did not report a unique denominator of Sn isotope ratios (De Laeter and Jeffery, 1965, 1967; Devillers *et al.*, 1983;
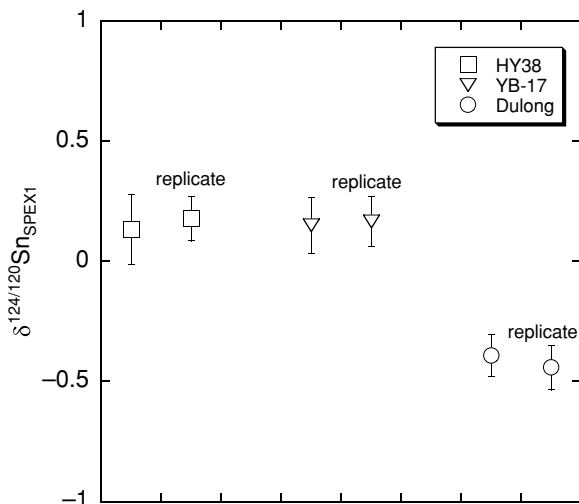
Fig. 4. Replicates for three cassiterite samples from China. The "replicate" represents samples stored for one month. δ-values are corrected for isotopic variation in the purification process. Data show the average of three measurements, and uncertainties are 2SD.

Rosman *et al.*, 1984; Rosman and McNaughton, 1987; Loss *et al.*, 1990; McNaughton and Loss, 1990; McNaughton and Rosman, 1991; Lee and Halliday, 1995; Gale, 1997; Clayton *et al.*, 2002; Moynier *et al.*, 2009; Osawa *et al.*, 2009; Haustein *et al.*, 2010; Nickel *et al.*, 2011). In this study, we chose the most abundant isotope, ^{120}Sn, as the denominator of isotope pairs. Because we monitored seven Sn isotopes by MC-ICP-MS (114, 116, 117, 118, 120, 122, 124), six isotope ratios are obtained in a single analysis (^{114}Sn/^{120}Sn, ^{116}Sn/^{120}Sn, ^{117}Sn/^{120}Sn, ^{118}Sn/^{120}Sn, ^{122}Sn/^{120}Sn, and ^{124}Sn/^{120}Sn). For comparison with previous studies that did not measure ^{120}Sn (Haustein *et al.*, 2010), we also report two isotope ratios, ^{122}Sn/^{116}Sn and ^{124}Sn/^{116}Sn.

The results of one single-day analysis for the eight isotope ratios are presented in Fig. 2, together with the average of individual ratios over the entire analytical period. The single-day data are the result of a measurement for SRM 3161a in a day, where the uncertainty represents the within-run analytical precision (2SE of 100 data collection with 5% rejection). The uncertainty of the grand mean represents 2SD of the multiple single-day data during this study. As shown in Fig. 2, the Sn isotopic composition of SRM 3161a is enriched in lighter isotopes compared to the in-house standard solution, SPEX1. The within-run precision for each ratio was better than 0.04‰ (2SE), with the exceptions of ^{114}Sn/^{120}Sn, ^{122}Sn/^{116}Sn, and ^{124}Sn/^{116}Sn. The overall reproducibility of SRM 3161a measurements over two months was better than 0.10‰, excluding ^{114}Sn/^{120}Sn. The result is comparable to the external reproducibility of Sn isotope analysis reported

Table 5. Tin isotope measurements for cassiterite samples. These δ-values were corrected for the modification of isotopic ratios by our purification process. We prepared five batches for M22545, and the result shown below is the average value.

	Sample	$\delta^{124/120}$Sn [‰]	2SD
Japan	KN1979	−0.04	0.11
	M21406	−0.03	0.10
	M21797	−0.10	0.13
	M22550	−0.08	0.12
	M22561	0.17	0.11
	M. Kano	−0.23	0.10
	M22545	0.20	0.08
	Average	−0.02	0.31
China	HY38	0.09	0.16
	GL1	0.34	0.12
	KM3	−0.14	0.10
	KM08-1	−0.05	0.12
	YB-17	0.11	0.13
	Gejiu	−0.19	0.11
	Dulong	−0.44	0.10
	Average	−0.04	0.50
Thailand	Yod Nam	0.04	0.11
	77120503-2	0.01	0.10
	77120503-3	−0.03	0.10
Malaysia	780326-5	0.07	0.11
	Average	0.02	0.09

by Moynier *et al.* (2009). In both the internal and the external precisions, ^{114}Sn/^{120}Sn showed the greatest uncertainties, whereas ^{118}Sn/^{120}Sn was marked by the lowest uncertainties, simply reflecting the counting statistics controlled by isotope abundances.

It is generally accepted that the extent of mass fractionation during ICP-MS analyses is a function of not only the difference of-, but also the average of masses between target and reference isotopes (Clayton *et al.*, 2002). Then, ^{124}Sn/^{120}Sn is the pair whose average is equivalent to the two Sb isotopes (^{121}Sb and ^{123}Sb) used for the external correction. Thus, in the following discussion, we use the ^{124}Sn/^{120}Sn ratio for our sample data unless otherwise indicated.

Evaluation of Sn isotope shift in column chemistry

In this section, we evaluate the shift in Sn isotopic ratios obtained by MC-ICP-MS analysis for samples purified by passing through TRU resin. There are two potential sources that can shift the observed Sn isotopic compositions: 1) isotopic fractionation during column chemistry due to incomplete Sn recovery; and 2) matrix effect in MC-ICP-MS analysis caused by organic material coexisting in the Sn fraction derived from TRU resin.
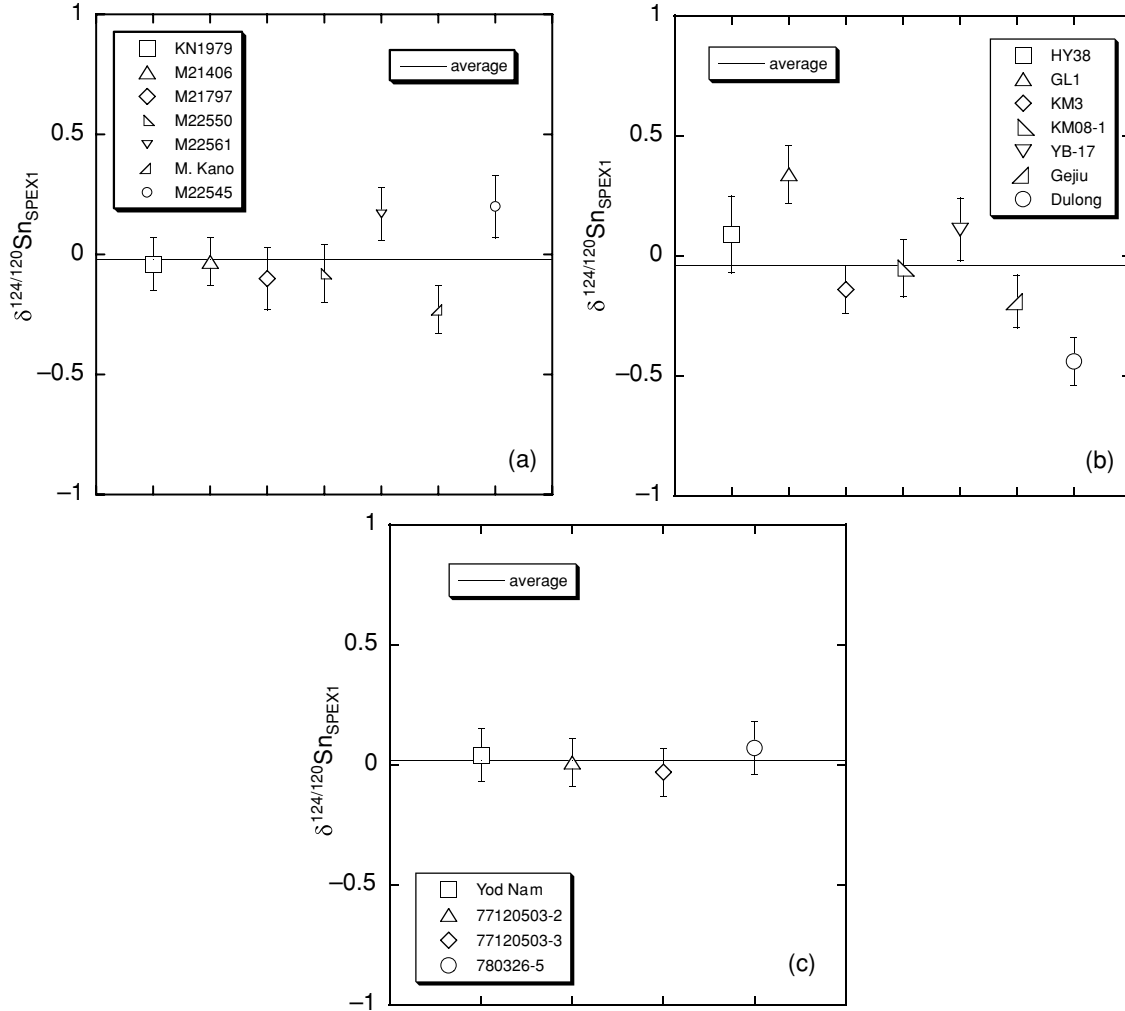
Fig. 5. Tin isotope analysis for cassiterite samples. (a) Japan: Isotope measurements were carried out three times for each. However, for M22545 (Naegi district), we prepared five batches and performed analysis three times. Uncertainties are all 2SD. The solid line represents the average value of samples. (b) China. (c) Thailand and Malaysia.

The latter is rather serious because the presence of organic substances in a sample solution increases the viscosity of the solution and may lead to modification of isotopic ratios in MC-ICP-MS analysis.

The isotopic shift in Sn during column chemistry was tested by passing the SPEX2 or MIX50 solution through TRU resin. In both experiments, solutions containing 1500 ng of tin were used. Recoveries of Sn were better than 95%. The results are summarized in Table 4. $\delta^{124/120}Sn_{SPEX1}$ of SPEX2, determined as $-0.04 \pm 0.03‰$ ($n = 5$), was used for calculating isotopic shifts during purification. Five different batches of SPEX2 were separately purified by passing through TRU resin, and showed significant Sn isotopic shifts that were reproducible within analytical uncertainties ($\delta^{124/120}Sn_{SPEX1} = -0.65 \pm 0.09‰$; Fig. 3a and Table 4). A test using the MIX50 resulted in

identical isotopic shift within error ($\delta^{124/120}Sn_{SPEX1} = -0.67 \pm 0.08‰$). It should be noted that these results differ from those of Haustein *et al.* (2010), who reported no isotopic shift during chemical purification with TRU resin. In this study, we take the overall average of the isotopic shifts listed in Table 4 ($-0.66 \pm 0.09‰$) as the correction factor in MC-ICP-MS analysis for all the samples purified by TRU resin.

The repeatability of isotopic shift through column chemistry was also examined using 1 mg of a cassiterite sample from Naegi district, Japan. After sample digestion, 80% of the cassiterite solution was split into five aliquots and used for separation, while the rest was used to confirm the Sn concentration. All separations were performed within a single day, and >96% of Sn recovery was confirmed for all samples. The Sn isotope analysis
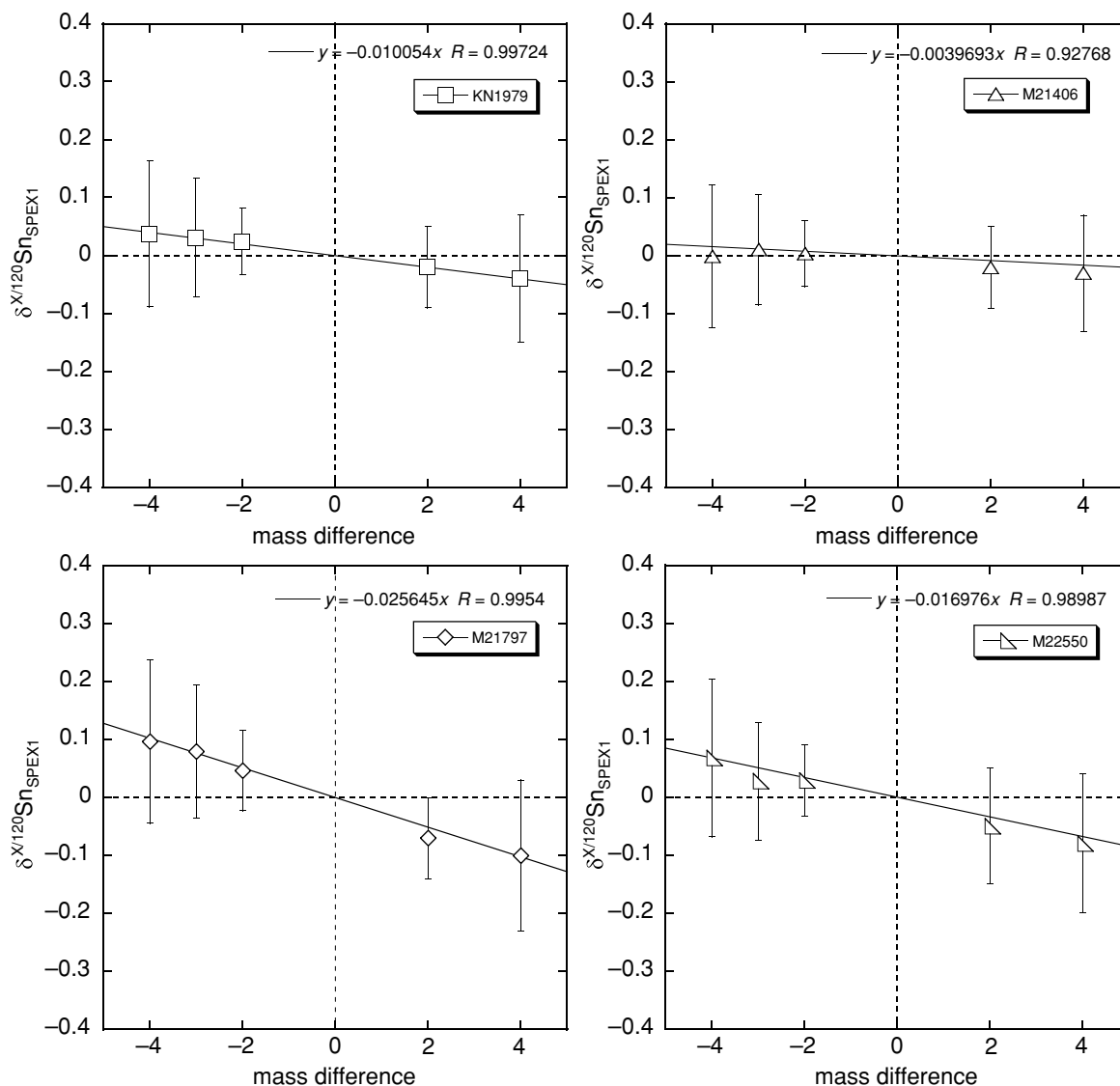
Fig. 6. Mass-dependent fractionation of cassiterite samples in Japan. Delta values of each mass pair are shown in the following graphs. $^{114/120}Sn$ was excluded because of the mass interference of Cd. Other than "M22545," measurements were carried out three times. Five batches of solutions were analyzed for M22545 to evaluate repeatability. We analyzed each solution three times; the results below represent the average of all measured data for M22545. Analytical errors are 2SD. Solid lines indicate regression lines passing through the origins.

by MC-ICP-MS was carried out within a week after the separation. As illustrated in Fig. 3b, we obtained a uniform $\delta^{124/120}Sn_{SPEX1}$ of $-0.42 \pm 0.09‰$. The reproducibility of the five measurements is comparable to the results of SPEX2 purification (Fig. 3a). It is therefore likely that the difference in matrix of loading solutions has no significant effect on the repeatability regarding the extent of apparent Sn isotopic shift during purification.

We also examined whether Sn isotope composition in digested cassiterite solutions dissolved in 30% HCl differed after long-term storage. Three Chinese cassiterite

solutions (HY38, YB-17, and Dulong) that were purified after one-month storage were used for this test (Fig. 4). Replicate analyses gave consistent isotope compositions within the known uncertainties, demonstrating that long-term (at least one month) storage of decomposed cassiterite solutions would not shift the Sn isotopic compositions as measured by MC-ICP-MS.

Effect of organic matter in Sn fraction

To further evaluate the reason for the observed Sn isotopic shift, we evaluated the influence of organic materi-
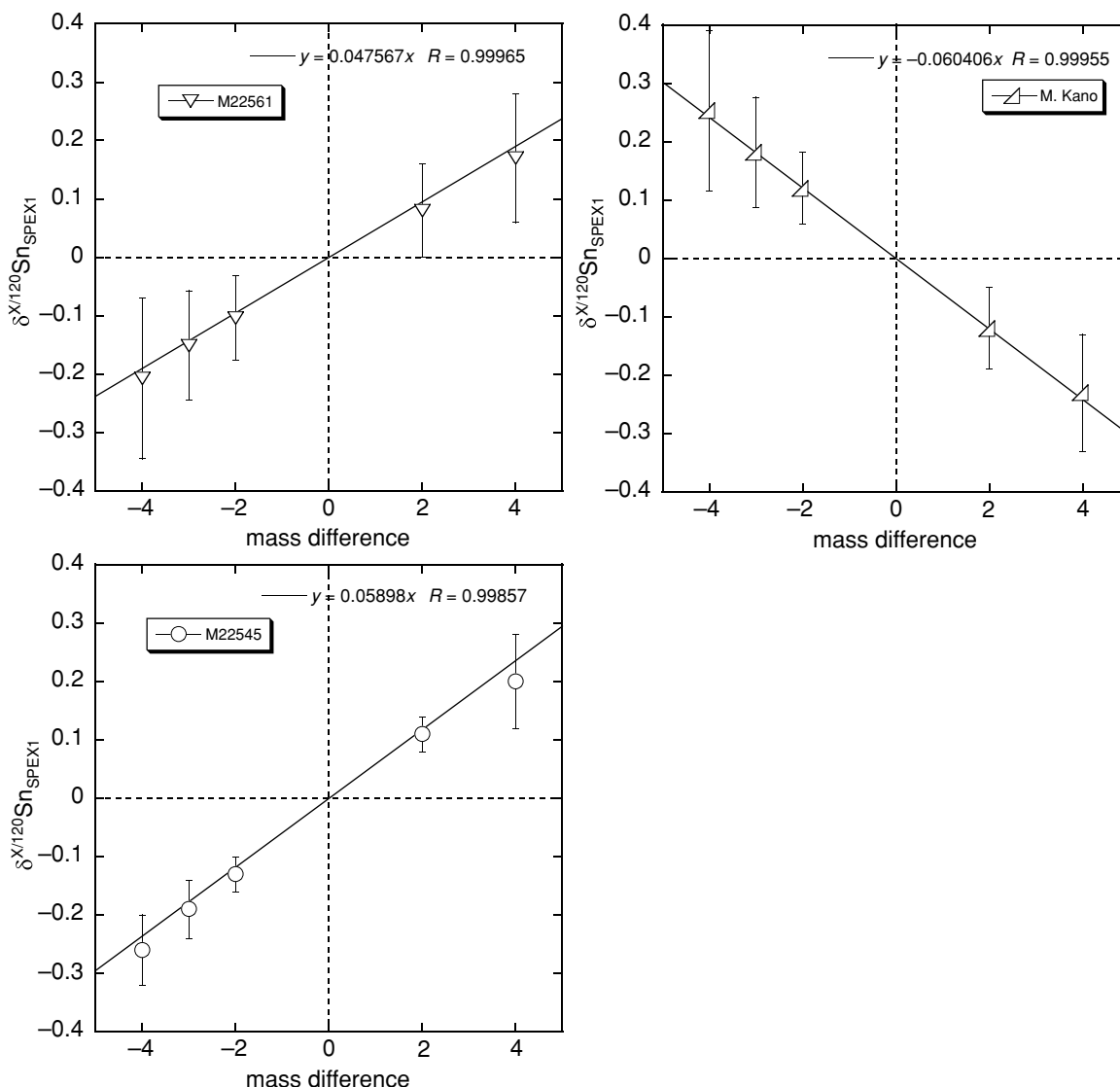
Fig. 6. (continued).

als in the Sn fraction that were derived from TRU resin. We loaded blank HCl solution to TRU resin, and recovered the Sn fraction as described in Table 1, to which SPEX1 was added. The Sn isotope compositions in this solution were markedly different from the original SPEX1 ($\delta^{124/120}Sn_{SPEX1} = -0.37 \pm 0.03‰$, the error was 2SE.), suggesting that the coexistence of organic matter caused an apparent Sn isotopic shift. Interestingly, the observed shift does not match the correction factor for the isotopic shift obtained by the purification test using SPEX2 and MIX50 ($-0.66 \pm 0.09‰$; Table 4). This implies that other factors (e.g., incomplete Sn recovery) also play an important role in shifting the observed Sn isotope ratios.

In general, the amounts of organic substances from chromatographic resins present in the sample fraction can be reduced by heating the sample with oxidative acids such as $HClO_4$ and HNO_3. However, the method cannot be applied in Sn analysis because it would oxidize Sn and may cause isotope fractionation by forming insoluble oxides. Consequently, all the samples purified by TRU in this study were analyzed without eliminating organic matter from the Sn fraction. Thus, the correction factor determined above is used to correct for multiple processes related to column chemistry, all of which can cause isotopic shift.

Tin isotope analysis for cassiterite samples

We analyzed 18 cassiterite samples collected from Southeast and East Asian countries (Japan, China, Thailand, and Malaysia; Table 1). The Sn contents of most of

the samples ranged from 30% to 50%. The results of $\delta^{124/120}Sn_{SPEX1}$ for the cassiterite samples are listed in Table 5 and shown in Fig. 5. As discussed in the previous section, all the data reported here are corrected for the isotopic shift occurring during sample purification (i.e., $-0.66 \pm 0.09‰$). We purified cassiterite solutions containing 1500 ng of tin, and confirmed that recovery of tin was better than 95%. The loading amount and recovery of tin were consistent with those observed in tests to evaluate isotope shift during sample purification. In addition, we confirmed that elements absent from the MIX50 solution were only present in the cassiterite samples at trace levels. Thus, we postulate that the observed shift for SPEX2 and MIX50 can also be applied to the correction for cassiterite sample solutions. The uncertainty in the correction factor propagated into the uncertainty in individual isotope ratios.

Significant Sn isotopic variations are observed in cassiterite samples from Japan and China, whereas samples from Thailand and Malaysia have a homogeneous Sn isotopic composition. As shown in Fig. 5a, two cassiterites of M22561 (Takatori mine, Ibaraki) and M22545 (Naegi district, Gifu) are enriched in heavier isotopes, while one from M. Kano (Kano mine, Miyazaki) is enriched in lighter isotopes. Other Japanese samples have isotopic compositions between the two groups. The results for Chinese cassiterites are shown in Fig. 5b. Four samples from Xinjiang (HY38, GL1, KM3, and KM08-1) show relatively large isotopic variation that exceeds the analytical errors. The differences between the maximum and minimum $\delta^{124/120}Sn_{SPEX1}$ values in Japanese and Chinese cassiterites are 0.44‰ and 0.77‰, respectively. All the data are plotted on the theoretical mass fractionation line (Fig. 6 shows examples of $\delta^{X/120}Sn_{SPEX1}$ vs. mass difference for cassiterite samples in Japan), and mass-independent fractionation was not observed. Moynier *et al.* (2009) observed mass-independent fractionation in liquid-liquid extraction with dicyclohexano-18-crown-6. Malinovskiy *et al.* (2009) also observed mass-independent fractionation in synthesis and decomposition of methyltin under UV irradiation. In both reports, odd isotopes showed mass-independent behaviors, while even isotopes showed mass-dependent behaviors. We did not observe mass-independent fractionation in ^{117}Sn in cassiterites in this study.

Tin isotopic variations for cassiterite have been investigated over the past 50 years (De Laeter and Jeffery, 1965, 1967; McNaughton and Loss, 1990; McNaughton and Rosman, 1991; Haustein *et al.*, 2010). The results of early studies (De Laeter and Jeffery, 1965, 1967) had poor analytical uncertainties of approximately 0.1% per atomic unit, which were too large to discuss possible isotopic fractionation in nature. McNaughton and Rosman (1991) analyzed Sn isotope compositions of five cassiterite samples by TIMS with the use of a double spike. They found no significant isotopic fractionations among cassiterite samples, except one sample that showed a fractionation of 0.15‰ (per atomic unit) to their laboratory standard. The authors left the cause of the isotopic fractionation unsolved. It is possible that the reason they could not find natural variations for most of their samples was because the analytical error of some samples reached 0.3‰ per atomic unit, which is ten times worse than that of recent MC-ICP-MS studies.

More recently, Haustein *et al.* (2010) reported a variation as large as 0.55‰ per unit mass difference in Sn isotopic compositions, which corresponds to 2.2‰ difference in $\delta^{124/120}Sn$, for cassiterite samples from Cornwall and Erzgebirge regions, Europe. Because there is no international isotope standard material for Sn, we cannot compare our results directly with previous studies. This variation, however, is approximately three times greater than our results for cassiterites from China. Although further work is needed, it can be suggested at this point that the extent of Sn isotope variation in cassiterites from the Southeast and East Asian regions is smaller than in European samples. Haustein *et al.* (2010) also observed significant isotopic variations in samples from a single ore deposit, and suggested the existence of variable formation conditions (e.g., temperature, pressure, etc.) in individual deposits. In this study, two samples from the Kamst deposit in China (KM3 and KM08-1) showed identical isotope compositions within the uncertainties. Two samples from the Kosaba mine in Thailand (77120503-2 and 77120503-3) also showed consistent isotope compositions. Although the results are based on a small number of samples, the findings do not support the existence of multiple physicochemical conditions within a single ore deposit that may result in detectable Sn isotopic fractionation.

McNaughton and Rosman (1991) proposed three possible mechanisms for Sn isotopic fractionation: 1) equilibrium fractionation between Sn oxide and sulfide minerals; 2) kinetic fractionation, which could take place during dissolution of Sn in a source region and precipitation of Sn in an ore deposit; and 3) multistage enrichment process of Sn from crustal material to ore, in which each step introduces kinetic fractionation. It is difficult to conclude the cause of isotopic fractionation observed in cassiterite samples analyzed in this study; however, we can suggest the following points. Among the deposits from which the analyzed cassiterites were sampled, Ikuno, Kaneuchi, Ohtani, and Kiwada mines were reported to contain stannite, a tin sulfide. Stannite was also confirmed under microscope observation of thin sections from Takatori mine. There is no description for stannite in Kano and Naegi mines (Takimoto, 1944). Although it has not been investigated whether cassiterites precipitated in equi-

librium with the observed tin sulfide minerals, we suggest that the presence of tin sulfide minerals does not play an important role for Sn isotope fractionation in Japanese cassiterites. As shown in Fig. 5c, cassiterite samples from Southern Thailand and Malaysia have a homogeneous Sn isotopic composition. Cassiterites from Yod Nam mine form veins with quartz, suggesting a high-temperature origin, whereas cassiterite veins in Kosaba mine co-exist with low-temperature minerals (Ishihara *et al.*, 1980). Therefore, the observed homogeneous isotope compositions in Southern Thailand and Malaysian cassiterites suggest that the temperature during ore formation was not the main cause of Sn isotope variation. This would exclude the second hypothesis, above. As for the third hypothesis, we have only limited Sn abundance and isotope data for possible source rocks of cassiterite deposits on which to base quantitative discussion of Sn isotope fractionation during the interaction between ore deposits and surrounding crust.

Table 1 summarizes geochronological information on Sn mineralization and host rock formation. It is unlikely that the Sn isotope compositions of the cassiterites correlate with the ages of their host rocks. Further studies are required to reveal the cause of Sn isotope fractionation in cassiterites.

CONCLUSIONS

We have developed a new analytical technique for precise Sn isotope measurement in cassiterites using MC-ICP-MS, which includes a sample decomposition method employing hydroiodic acid and a subsequent Sn purification procedure using an extraction chromatographic resin, TRU. We found that Sn purification using TRU resin caused an apparent Sn isotopic shift, most likely because of the inclusion of organic material in the Sn fraction, but that other factors (e.g., incomplete Sn recovery) also played a role in the shift. Repeated analyses of Sn solutions confirmed consistent apparent Sn isotopic shift during purification. This enables the correction of Sn isotope measurement in MC-ICP-MS for samples purified by passing through TRU resin. We carried out a series of Sn isotope analyses by MC-ICP-MS for 18 cassiterite samples from Japan, China, Thailand, and Malaysia. Significant isotopic variations were detected in cassiterite samples from Japan and China, although the variation was smaller than those observed in cassiterites from Europe (Haustein *et al.*, 2010). The mechanism of isotopic fractionation is still unclear.

REFERENCES

Adachi, T. (1997) Mitate mine and Kano mine. *Melange (Research Group for Applied Geology in Miyazaki)* **8**, 29–45 (in Japanese).

Bignell, J. D. and Snelling, N. J. (1977) *Geochronology of Malayan Granites. Overseas Geol. Min. Resuor.* **47**, Institute of Geological Sciences, 72 pp.

Budd, P., Haggerty, R., Pollard, A. M., Scaife, B. and Thomas, R. G. (1995) New heavy isotope studies in archaeology. *Isr. J. Chem.* **35**, 125–130.

Burbidge, E. M., Burbidge, G. R., Fowler, W. A. and Hoyle, F. (1957) Synthesis of the elements in stars. *Rev. Mod. Phys.* **29**, 547–654.

Caley, E. R. (1932) The action of hydriodic acid on stannic oxide. *J. Am. Chem. Soc.* **54**, 3240–3243.

Chen, F., Li, H., Cai, H., Liu, H. and Chang, H. (1999) Chronology and origin of the Ganliangzi tin orefield, Xinjiang. *Mineral Deposits* **18**, 91–97 (in Chinese with English abstract).

Chen, J., Halls, C. and Stanley, C. J. (1992) Tin-bearing skarns of South China: Geological setting and mineralogy. *Ore Geol. Rev.* **7**, 225–248.

Clayton, R., Andersson, P., Gale, N. H., Gillis, C. and Whitehouse, M. (2002) Precise determination of the isotopic composition of Sn using MC-ICP-MS. *J. Anal. At. Spectrom.* **17**, 1248–1256.

Cobbing, E. J., Pitfield, P. E. J., Darbyshire, D. P. F. and Mallick, D. I. J. (1992) *The Granites of the South-East Asian Tin Belt. British Geol. Surv., Overseas Mem.* **10**, 369 pp.

Council of Underground Resources Development (1956) *Unused Iron Resources*, Vol. 2, 418–430 (in Japanese).

De Laeter, J. R. and Jeffery, P. M. (1965) The isotopic composition of terrestrial and meteoritic tin. *J. Geophys.* **70**, 2895–2903.

De Laeter, J. R. and Jeffery, P. M. (1967) Tin: its isotopic and elemental abundance. *Geochim. Cosmochim. Acta* **31**, 969–985.

De Laeter, J. R., McCulloch, M. T. and Rosman, K. J. R. (1974) Mass spectrometric isotope dilution analyses of tin in stony meteorites and standard rocks. *Earth Planet. Sci. Lett.* **22**, 226–232.

De Laeter, J. R., Böhlke, J. K., De Biévre, P., Hidaka, H., Peiser, H. S., Rosman, K. J. R. and Taylor, P. D. P. (2003) Atomic weights of the elements: Review 2000. *Pure Appl. Chem.* **75**, 683–800.

Devillers, C., Lecomte, T. and Hagemann, R. (1983) Absolute isotope abundances of tin. *Int. J. Mass Spectrom. Ion Phys.* **50**, 205–217.

Gale, N. H. (1997) The Isotopic composition of tin in some ancient metals and the recycling problem in metal provenancing. *Archaeometry* **39**, 71–82.

Hall, A. (1980) The determination of total tin content of some geological materials by atomic absorption spectrophotometry. *Chem. Geol.* **30**, 135–142.

Haraguchi, K. and Kikuchi, T. (1952) Tungsten deposit in

Kaneuchi mine, Kyoto prefecture. *Bull. Geol. Surv. Japan* **3**, 465–469 (in Japanese with English abstract).

Haustein, M., Gillis, C. and Pernicka, E. (2010) Tin isotopy—A new method for solving old questions. *Archaeometry* **52**, 816–832.

Horwitz, E. P., Chiarizia, R., Dietz, M. L. and Diamond, H. (1993) Separation and preconcentration of actinides from acidic media by extraction chromatography. *Anal. Chim. Acta* **281**, 361–372.

Ikeda, N., Hida, H., Noguchi, K. and Fujiwara, M. (1983) Geology and ore deposits of the Takatori tungsten mine, Ibaraki Prefecture, Central Japan, with special reference to the fracture system. *Mining Geol.* **33**, 97–114 (in Japanese with English abstract).

Imai, H., Kim, M. S. and Fujiki, Y. (1972) Geologic structure and mineralization of the hypothermal or pegmatitic tungsten vein-type deposits at the Ohtani and Kaneuchi mines, Kyoto prefecture, Japan. *Mining Geol.* **22**, 371–381 (in Japanese with English abstract).

Ishihara, S. and Wu, C. (2001) Genesis of Late Cretaceous–Paleogene granitoids with contrasting chemical trends in the Chubu district, Central Japan. *Bull. Geol. Surv. Japan* **52**, 471–491.

Ishihara, S., Sawata, H., Shibata, K., Terashima, S., Arrykul, S. and Sato, K. (1980) Granites and Sn-W deposits of Peninsular Thailand. *Mining Geol. Spec. Issue* **8**, 223–241.

Kragten, J. (1975) The complexometry of tin (IV). *Talanta* **22**, 505–510.

Lee, D.-C. and Halliday, A. N. (1995) Precise determinations of the isotopic compositions and atomic weights of molybdenum, tellurium, tin and tungsten using ICP magnetic sector multiple collector mass spectrometry. *Int. J. Mass Spectrom. Ion Processes* **146/147**, 35–46.

Li, X. (1988) Geological characteristics of the tin deposits of China and the basic methods of prospecting and exploration. *Geology of Tin Deposits in Asia and the Pacific* (Hutchison, C. S., ed.), 306–315, Mineral Concentrations and Hydrocarbon Accumulations in the ESCAP Region Volume 3, Springer-Verlag.

Lide, D. R. (ed.) (1993–1994) *CRC Handbook of Chemistry and Physics*, 74th ed. CRC Press, New York.

Liw, T. C. and Page, R. W. (1985) U–Pb zircon dating of granitoid plutons from the West Coast Province of Peninsular Malaysia. *J. Geol. Soc. Lond.* **142**, 515–526.

Longerich, H. P., Freyer, B. J. and Strong, D. F. (1987) Determination of lead isotope ratios by inductively coupled plasma-mass spectrometry (ICP-MS). *Spectrochim. Acta B Atom. Spectros.* **42**, 39–48.

Loss, R. D., Rosman, K. J. R. and De Laeter, J. R. (1990) The isotopic composition of zinc, palladium, silver, cadmium, tin, and tellurium in acid-etched residues of the Allende meteorite. *Geochim. Cosmochim. Acta* **54**, 3525–3536.

Malinovskiy, D., Moens, L. and Vanhaecke, F. (2009) Isotopic fractionation of Sn during methylation and demethylation. *Environ. Sci. Technol.* **43**, 4399–4404.

McNaughton, N. J. and Loss, R. D. (1990) Stable isotope variations of tin. *Stable Isotopes and Fluid Processes in Mineralization* (Herbert, H. K. and Ho, S. E., eds.), 269–276, Geol. Dept. & Univ. Ext., Univ. W. Australia.

McNaughton, N. J. and Rosman, K. J. R. (1991) Tin isotope fractionation in terrestrial cassiterites. *Geochim. Cosmochim. Acta* **55**, 499–504.

Mei, Y., Li, H., Wang, D., Lu, Y., Yang, H., Xu, J. and Zhang, J. (2007) Rock-forming and ore-forming ages of the Yanbei porphyry tin deposit in Jiangzi province and their geological significance. *Acta Geoscientica Sinica* **28**, 456–461 (in Chinese with English abstract).

Ministry of International Trade and Industry of Japan (1987) *Report on Regional Geological Survey in the Bantan District.* 62 pp. (in Japanese).

Moynier, F., Fujii, T. and Télouk, P. (2009) Mass-independent isotopic fractionation of tin in chemical exchange reaction using a crown ether. *Anal. Chm. Acta* **632**, 234–239.

Nagahara, M. (1978) Geology, ore deposits and some guides to prospecting of the Kiwada tungsten mine, Yamaguchi prefecture. *Mining Geol.* **28**, 373–384.

Nickel, D., Haustein, M., Lampke, T. and Pernicka, E. (2011) Identification of forgeries by measuring tin isotopes in corroded bronze objects. *Archaeometry* **54**, 167–174.

Osawa, T., Ono, M., Esaka, F., Okayasu, S., Iguchi, Y., Hao, T., Magara, M. and Mashimo, T. (2009) Mass-dependent isotopic fractionation of a solid tin under a strong gravitational field. *EPL* **85**, 64001.

Park, C. F. and MacDiarmid, R. A. (1964) Xenothermal deposits. *Ore Deposits (A Series of Books in Geology)* (Gilluly, J. and Woodford, A. O., eds.), 346–355, W.H. Freeman and Company.

Qin, D., Li, Y., Tan, S., Chen, A., Xue, C., Fan, Z., Dang, Y., Tong, X., Wu, J., Li, Y. and Wang, H. (2006) Metallogenic ages of Gejiu tin ore deposit in Yunnan Province. *Chinese Journal of Geology* **41**, 122–132 (in Chinese with English abstract).

Rosman, K. J. R. and McNaughton, N. J. (1987) High-precision measurement of isotopic fractionation in tin. *Int. J. Mass Spectrom. Ion Processes* **75**, 91–98.

Rosman, K. J. R., Loss, R. D. and De Laeter, J. R. (1984) The isotopic composition of tin. *Int. J. Mass Spectrom. Ion Processes* **56**, 281–291.

Russell, W. A., Papanastassiou, D. A. and Tombrello, T. A. (1978) Ca isotope fractionation on the Earth and other solar system materials. *Geochim. Cosmochim. Acta* **42**, 1075–1090.

Saeki, K., Nakatani, N., Hai, T. and Tanabe, S. (1998) Determination of the total tin in biological materials by ICP-MS. *Bunseki Kagaku* **47**, 135–139 (in Japanese with English abstract).

Sear, L. G. (1997) The fusion of difficult materials including chromite, cassiterite and reduced sulphur. *X-Ray Spectrom.* **26**, 105–110.

Shen, W. and Ling, H. (1994) Isotopic geochemical characteristics and material sources of tin-bearing granite porphyry in Yanbei and Tashan. *Acta Geoscientia Sinica* **1–2**, 117–123 (in Chinese with English abstract).

Shen, W., Wang, D., Liu, C., Xiong, X. and Lai, M. (1996) Characteristics and origin of the Yanbei porphyry tin deposit. *Geological Journal of Universities* **2**, 85–91 (in Chinese with English abstract).

Shibata, H. (1939) Granitic rock and pegmatites at Naegi dis-

trict, Ena County, Mino Province. Part 3. *Jour. Geol. Soc. Japan* **46**, 547–559 (in Japanese).

Shibata, K. and Ishihara, S. (1974) K–Ar ages of the major tungsten and molybdenum deposits in Japan. *Econ. Geol.* **69**, 1207–1214.

Shibata, K., Miller, J. A., Yamada, N., Kawata, K., Murayama, M. and Katada, M. (1962) Potassium–argon ages of the Inagawa granite and Naegi granite. *Bull. Geol. Surv. Japan* **13**, 317–320 (in Japanese with English abstract).

Su, Y.-P., Tang, H.-F., Sylvester, P. J., Liu, C.-Q., Qu, W.-J., Hou, G.-S. and Cong, F. (2007) Petrogenesis of Karamaili alkaline A-type granites from East Junggar Xinjiang (NW China) and their relationship with tin mineralization. *Geochem. J.* **41**, 341–357.

Suzuki, K., Morishita, T., Kajizuka, I., Nakai, Y., Adachi, M. and Shibata, K. (1994) CHIME ages of monazites from the Ryoke metamorphic rocks and some granitoids in the Mikawa–Tono area, central Japan. *Bull. Nagoya Univ. Furukawa Museum* **10**, 17–38.

Takimoto, K. (1944) Studies on the tin deposits of Japan. *Japan. Jour. Geol. Geogr.* **19**, 195–241.

Tanaka, T., Mori, H. and Sasaki, K. (1971) Geology and ore deposits of the Ikuno mine, with Special reference to the gold-silver veins. *Mining Geol.* **21**, 162–173 (in Japanese with English abstract).

Tang, H. F., Qu, W. J., Su, Y. P., Hou, G. S., Du, A. D. and Cong, F. (2007) Genetic connection of Sareshike tin deposit with the alkaline A-type granites of Sabei body in Xinjiang:
constraint from isotopic age. *Acta Petrol. Sinica* **23**, 1989–1997 (in Chinese with English abstract).

Tang, H.-F., Su, Y.-P., Qiu, H.-N. and Han, Y.-J. (2009) [40]Ar–[39]Ar age of tin mineralization in the Beilekuduk tin metallogenic belt, East Junggar, Xinjiang (NW China). *Acta Petrol. Sinica* **25**, 1303–1309 (in Chinese with English abstract).

Wang, Z. (1983) Some problems on the mineralization of tin deposits in Gejiu, Yunnan. *Acta Geol. Sinica* **2**, 154–163 (in Chinese with English abstract).

Xiong, X., Zhu, J., Liu, C. and Shen, W. (1994) Alteration zoning of the Yanbei porphyry tin deposit in Jiangxi province and geochemical characteristics of its main altered rocks. *Mineral Deposits* **13**, 1–10 (in Chinese with English abstract).

Xu, K. and Zhu, J. (1988) Time-space distribution of tin/tungsten deposits in south China and controlling factors of mineralization. *Geology of Tin Deposits in Asia and the Pacific* (Hutchison, C. S., ed.), 265–277, Mineral Concentrations and Hydrocarbon Accumulations in the ESCAP Region Volume 3, Springer-Verlag.

Yi, E., Halliday, A. N., Lee, D.-C. and Christensen, J. N. (1995) Indium and tin in basalts, sulfides, and the mantle. *Geochim. Cosmochim. Acta* **59**, 5081–5090.

Zhang, H., Luo, T., Gao, Z., Ma, D. and Tao, Y. (2007) Helium, lead and sulfur isotope geochemistry of the Gejiu Sn–polymetallic ore deposit and the sources of ore-forming materials. *Chinese Journal of Geochemistry* **26**, 439–445.