Determination of natural isotopic variation in antimony using inductively coupled plasma mass spectrometry for an uncertainty estimation of the standard atomic weight of antimony

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The isotopic variation of industrially produced antimony was estimated using multiple-collector inductively coupled plasma mass spectrometry. A reproducible 123 Sb/ 121 Sb ratio of $\pm 0.004\%$ (2 standard deviations) was routinely obtained using a Sn doping mass discrimination correction technique. Only a small isotopic variation of about 0.05% was observed among industrially important Sb materials (five commercially available reagents and two ore minerals). The degree of Sb isotopic variation to determine the uncertainty in Sb atomic weight can be reduced by this new analytical technique to 0.00025 compared to the currently accepted IUPAC isotopic variation determined by conventional mass spectrometry of ± 0.001 . Heavy isotope enrichment of Sb in a drainage water sample from a stibnite mining area was found. This heavy isotope enrichment tendency in an aqueous environment may be useful in detecting anthropogenic Sb input from industrial emission by the smelting process via air because Sb of anthropogenic origin will have lighter isotope enrichment features.

Keywords: Sb isotope ratios, multiple collector ICP-MS, element doping technique, natural isotopic variation, standard atomic weight concept

INTRODUCTION

Antimony (Sb) is a metalloid element and a member of group 15 in the periodic table of the elements. The main industrial use of Sb is as Sb_2O_3 (about 2/3 of total consumption), which is added to plastics as a flame retardant and it is also used as a catalyst during the synthesis of plastics as well as in alloys for ammunition (Krachler *et al.*, 2001). Sb is frequently found around mining and smelter areas where it can be transported to the atmosphere as small particles after industrial emission upon which it enters aquatic and terrestrial systems (Filella *et al.*, 2002). The environmental chemistry of Sb is important since Sb and its compounds are considered to be pollutants of priority interest (Filella *et al.*, 2002).

Recently, the mass-dependent fractionation of stable isotope ratios of heavy elements has been applied to evaluate the environmental impact of human activity (Weiss *et al.*, 2008), in addition to isotopic variation by radiogenic decay (e.g., anthropogenic Pb; Bollhöfer and Rosman, 2001). As an example, the mass-dependent fractionation of zinc stable isotopes from a smelting process is potentially a new indicator of zinc pollution around the emission source (Sonke *et al.*, 2008). If such isotopic fractionation is recognized for Sb compounds in industrial purification process like zinc (Tanimizu *et al.*, 2002), their Sb isotope ratios may become a good indicator for the human activity. Actually Sb compounds are rather volatile and their anthropogenic enrichment in aerosols over natural sources is very high. The typical antimony concentration in aerosols is estimated to be <0.1 ng/m³ over the open ocean to several ng/m³ in industrial areas (Filella *et al.*, 2002).

Antimony has two stable isotopes, ¹²¹Sb and ¹²³Sb and their isotopic abundances are reported to be 57.21% and 42.79%, respectively, by IUPAC (Loss, 2003) based on a calibrated mass spectrometric analysis in 1993 (Chang *et al.*, 1993) to estimate atomic weight of Sb. The isotopic variation in industry-related Sb materials (five reagents and five ore minerals) was also estimated to evaluate practical uncertainty related to Sb atomic weight, and was uniform within a relative analytical uncertainty of $\pm 0.06\%$ (Chang *et al.*, 1993). Recently, a natural isotopic variation of Sb in various geological materials was estimated by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) with a relative precision of

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ICP ion source	
rf frequencies	27.12 MHz
rf power	1.2 kW forward, <1 W reflection
Fassel-type torch Ar gas flow rates	
outer	15 L/min
intermediate	0.70 L/min
central	1.15 L/min
nebulizer	Glass Expansion Micromist
spray chamber	dual sychronic/double Scott glass chamber (ambient temperature)
sample uptake	100 μ L/min (free aspiration)
Mass spectrometer	
ion energy	10000 V
extraction	2000 V
typical transmission	
Sb	30×10^{-11} A/ppm at low resolution
Pressures during operation	
ESA	$1.0-1.5 \times 10^{-5}$ Pa (9×10^{-6} Pa during standby)
Analyzer	$4-9 \times 10^{-7}$ Pa (4 × 10 ⁻⁷ Pa during srandby)

Table 1. Typical instrumental operation conditions. The central argon gas flow rate was adjusted to maximize the transmission of the Sb ion signal

±0.009%. A large isotopic fractionation between Sb(III) and Sb(V) in aqueous solutions was reported (Rouxel *et al.*, 2003). The Sb isotopic variation was, however, obtained from samples which included Sb as a minor element, and the Sb isotopic variation in industrial samples (reagents and ores), which are important to evaluate atomic weight of Sb, was still undetermined. In this study, the Sb isotopic variation was re-estimated as a basis for the detection of anthropogenic atmospheric Sb input into the environment, which should have a lighter isotope enrichment feature (Weiss *et al.*, 2008). The uncertainty in Sb atomic weight was re-evaluated from the isotopic variation because the atomic weight of polyisotopic elements and their uncertainty are calculated from their isotopic abundance and isotopic variation, respectively.

ANALYTICAL PROCEDURE

Mass spectrometry

In a previous MC-ICP-MS Sb isotopic study, samples were introduced into the instrument with a hydride generation system and a sample-standard bracketing technique was applied to correct for the time-dependent isotopic drift during the analysis (Rouxel *et al.*, 2003). The sample introduction efficiency of the hydride generation system is, however, dependent of sample matrix (82% recovery with matrix elements; Rouxel *et al.*, 2003), and low recovery less than 95% is a potential source of artificial isotopic fractionation in the analytical procedure. Moreover, sample-standard bracketing method can work only under a severe matrix matched condition among analytes (Malinovsky *et al.*, 2003; Tanimizu and Ishikawa,

2006). A Sn doping technique using conventional wet plasma was developed and used here, which enabled us to measure the Sb isotope ratios more precisely and accurately.

Isotope ratios were determined with a Neptune (Thermo Scientific, Bremen, Germany) at the Kochi Core Center. The details of this instrument has been described previously (Weyer and Schwieters, 2003; Wieser and Schwieters, 2005). The ion signal intensities of ¹²¹Sb and ¹²³Sb were detected simultaneously by multiple Faraday cups with those of ¹¹⁷Sn and ¹¹⁹Sn for the correction of the instrumental mass discrimination and ¹²⁵Te for the isobaric interference correction of ¹²³Te.

In the Sn doping technique developed here, observed 123 Sb/ 121 Sb isotope ratios were corrected by an exponential law using the 119 Sn/ 117 Sn ratio of a reference Sn solution, which was doped into the samples before the analysis. The relationship between the observed and normalized isotope ratios of Sn and Sb (R^{obs} and R^{norm} for 123 Sb/ 121 Sb and 119 Sn/ 117 Sn) is described by the following expression from the exponential law:

$$R_{123/121}^{\text{norm}} = R_{123/121}^{\text{obs}} \left(\frac{A_{123}}{A_{121}} \right)^{J_{\text{Sb}}}$$
(1)

$$R_{119/117}^{\text{norm}} = R_{119/117}^{\text{obs}} \left(\frac{A_{119}}{A_{117}}\right)^{f_{\text{Sn}}}$$
(2)

$$f_{\rm Sb} = f_{\rm Sn} \tag{3}$$

where *f* and *A* are the mass discrimination correction factor and the atomic masses of the Sn and Sb isotopes, respectively. The recommended 119 Sn/ 117 Sn ratio of 1.11849 (Loss, 2003) was used for normalization.

No international isotopic reference material is available for either elements and, therefore, we prepared reference solutions from two Spex 1000 μ g/mL concentration standards (Spex Certiprep., NJ, USA) for Sb and Sn. The 1000 μ g/mL Sb standard was diluted to 50 ng/mL with 2% HNO₃ and used for the isotopic analysis. The 1000 μ g/mL Sn solution was diluted to 10 μ g/mL with 1.2 M HCl and doped into the 50 ng/mL Sb solutions to produce a concentration of 50 ng/mL Sn just before analysis because of the instability of Sn ions in HNO₃ media.

Sample solutions were introduced with a 100 μ L/min flow GE Micromist nebulizer (Glass Expansion, Australia) in free aspiration mode attached to a dual cyclonic/ double Scott quartz glass chamber. From this wet plasma condition, we routinely achieved signal intensities larger than 3×10^{-10} A for 1 μ g/mL Sb using the X-type skimmer cone. The typical operating conditions of the instrument are shown in Table 1. Desolvating nebulizers are useful in enhancing the signal sensitivity but the difference in chemical behavior between the analyte and the doped element during the heating process may be problematic (Kamenov *et al.*, 2004). Because of the different chemical behavior between Sb and Sn, we used the conventional sample introduction method.

All solutions were prepared with 18.2 M Ω ·cm water produced by a Milli-Q Element system (MILLIPORE, MA, USA). All acid reagents used were commercially supplied high-purity reagents, TAMAPURE AA-100 (Tama Chemical, Japan).

The main potential mass spectrometric interference during the determination of ¹²³Sb/¹²¹Sb ratio in wet plasma mode is the hydrides of Sb and Sn in addition to the isobaric interference of ¹²³Te because both Sb and Sn tend to become volatile hydrides under reducing conditions. In our Sn doping technique, the mass spectral interference species are ¹²⁰SnH and ¹²²SnH on ¹²¹Sb and ¹²³Sb as well as ¹¹⁶SnH and ¹¹⁸SnH on ¹¹⁷Sn and ¹¹⁹Sn, respectively. The SnH/Sn ratios were estimated from a diluted solution of the 1000 μ g/mL Sn standard with 2% HNO₃. The resultant SnH/Sn ratio estimated from the ion signal intensity of the mass number 121 as ¹²⁰SnH/¹²⁰Sn was about 3×10^{-5} under wet plasma conditions and this is one order of magnitude larger than that of Pb isotopes (Tanimizu and Ishikawa, 2006). This interference is most serious for ¹²¹Sb, and the Sb/Sn ratio of the samples was kept constant to within 10% variability. The ratios of other polyatomic species, SbO/Sb and SbOH/Sb were less than 0.1%, and the isotopic fractionation between Sb and SbO in the ICP ionization process was negligible under our operational conditions.

Table 2. Antimony isotopic variation of man-made and natural products. Relative deviations from the Spex 1000 μ g/mL Sb solution are shown as epsilon Sb values. Uncertainties are twice standard deviation of three replicate analyses

Samples	Form and grade	ε^{123} Sb
Sb reagents		
1000 ppm solution	for chemical analysis	$+2.36\pm0.63$
Wako Pure Chemical		
1000 ppm solution	for chemical analysis	$+1.13\pm0.75$
Kanto Chemical		
SbCl ₃	crystal, special grade 98%	$+3.81\pm0.35$
Nakalai Tesque		
Sb_2O_3	powder, >99.999%	$+2.97\pm0.72$
Aldrich Chemical		
$K[Sb(OH)_6]$	powder, first grade	$+2.80\pm0.40$
Wako Pure Chemical		
Natural samples		
Stibnite #1		-0.97 ± 0.38
Ichinokawa mine, Japan		
Stibnite #2		$+0.30\pm0.38$
Ichinokawa mine, Japan		
drainage water		$+3.29\pm0.38$
Ichinokawa mine, Japan		

Samples

From the "standard" atomic weight concept (e.g., De Laeter et al., 1992), the isotopic variation among readily available industrial materials is important for the estimation of mean atomic weight and its related uncertainty. The Sb isotope ratios of the commercially available reagents of 1000 μ g/mL Sb solution, SbCl₃, Sb₂O₃, and $K[Sb(OH)_6]$ were determined. The 1000 μ g/mL solution reagents were from Wako Pure Chemical, Japan, Kanto Chemical, Japan, and Spex Certiprep, USA. These solutions are typically processed by dissolving purified Sb metal via Sb oxides and are representative of industrial Sb metal products. A high purity Sb₂O₃ reagent (Sigma-Aldrich, USA) and a Sb(V) reagent (K[Sb(OH)₆]; Wako Pure Chemical, Japan) were also included in the sample list to evaluate degrees of Sb isotopic fractionation in further purification process and oxidation process using smelted Sb₂O₃ products to make the reagents. The solid reagents, SbCl₃, Sb₂O₃, and K[Sb(OH)₆], were dissolved in ethanol (Wako Pure Chemical, special grade), 20% acetic acid (Tama Chemical, AA-100 grade), and Milli-O water respectively to obtain concentrations of about 1000 μ g/mL. Their chemical forms and chemical purities are listed in Table 2.

Stibnite (Sb_2S_3) is the primary ore of industrial Sb and its isotope ratio was determined to evaluate the degree of mass fractionation during the smelting process. Two stibnite samples were collected from mine dumps of the Ichinokawa mine, Japan for this purpose. The Ichinokawa mine is now abandoned but famous as having contained one of the largest known stibnite crystals (Bancroft, 1988). Specimens were dissolved with conc. HNO₃ to obtain concentrations of around 10000 μ g/mL Sb. In addition, a drainage water sample was collected at the entrance of the mine and was analyzed to evaluate the Sb isotopic behavior in an aqueous environment. The Sb concentration was determined using a Quadrupole ICP-MS (ELAN DRCII, Perkin Elmer Sciex, Toronto, Canada) to be about 0.3 μ g/mL (pH ~ 8.0). Antimony in these geological samples was purified with thiol cotton fiber (TCF) column in a similar manner as described previously (Yu *et al.*, 1983; Rouxel *et al.*, 2003).

All Sb sample solutions were diluted to 50 ng/mL with 2% HNO₃ and used for analysis. Trivalent Sb is stable only with ligands to form stable Sb(III) complexes, and quickly oxidized to Sb(V) under ambient oxic aqueous conditions in several hours (Zheng *et al.*, 2001). Therefore, the sample solutions were preserved under ambient conditions for several days to produce pentavalent Sb.

RESULTS AND DISCUSSION

The ¹²³Sb/¹²¹Sb isotope ratio of the 50 ng/mL Spex reagent after the mass discrimination correction with ¹¹⁹Sn/¹¹⁷Sn was 0.74692 \pm 0.00004 (*n* = 7; 2 × SD) in a same day analytical session. The isotope ratio is consistent within analytical uncertainty compared to the previous mass-discrimination corrected TIMS value of 0.74786 \pm 0.00098 (Chang *et al.*, 1993). A comparison of the two values is not so meaningful, however, because no comparable isotopic reference material is present in addition to the imperfect mass discrimination correction of the element doping technique in MC-ICP-MS (Albarède et al., 2004). The isotopic reproducibility of the Spex solution of $\pm 0.004\%$ in our isotopic analysis is much better than that of TIMS ($\pm 0.06\%$; 2 × SD) and hydride generation MC-ICP-MS analysis with the sample-standard bracketing technique ($\pm 0.009\%$; 2 × SD) (Rouxel *et al.*, 2003). Besides, Sb isotope ratios of reagent samples treated with TCF column gave typically 0.03–0.05% higher values using the sample-standard bracketing technique only, but their values using the Sn-doping technique were consistent with the values of untreated reagents within analytical uncertainty. This means that the sample-oriented matrix effect (organic material from TCF in this case) is effectively eliminated using the Sn-doping technique. Our MC-ICP-MS method requires about five times more sample amount compared to the previous MC-ICP-MS analysis but the influence of matrix elements which can induce isotopic drift is minimal. Highly reproducible determination of Sb isotopic variation among industrially important materials is possible using our analytical technique.



Fig. 1. Epsilon Sb values of man-made and natural products. Values for chemical reagents are plotted as open symbols while those for natural samples are plotted as closed symbols.

Since our isotopic analysis does not give absolute isotope ratios as mentioned above, the relative isotopic variation among samples is important for our purposes. The relative deviation of the samples from the Spex standard is summarized in Table 2 as epsilon values. The epsilon notation is a relative isotopic deviation of a sample from an isotopic standard in parts per 10^4 :

$$\varepsilon^{123} \text{Sb} = \left(\frac{\left(^{123} \text{Sb}/^{121} \text{Sb}\right)_{\text{sample}}}{\left(^{123} \text{Sb}/^{121} \text{Sb}\right)_{\text{standard}}} - 1\right) \times 10000.$$
(4)

The Sb isotope ratios of the reagents, which will have independent ore sources mutually, varied beyond the analytical uncertainty in a range of about four epsilons (Table 2). The Sb isotope ratios of the two stibnite samples have an almost consistent value compared to the Spex standard. No large Sb isotopic variation by ten epsilons reported between Sb(III) and Sb(V) equilibrium reaction and among hydrothermal sulfides (Rouxel et al., 2003) was observed. A possible explanation for this variation is that isotopic deviations from the uniform source material occur through the industrial purification process, typically in smelting and roasting processes (Sonke et al., 2008), which enriches the heavier isotope in products in various degrees as lighter Sb isotopes are lost as vapor. Alternatively, the detected small Sb isotopic variation (Table 2 and Fig. 1) may be inherited from a Sb isotopic heterogeneity of the source minerals produced in different geological settings and this might be reflected in the reagents. Our highly reproducible Sb isotope analysis enables the detection of small isotopic mass fractionation among industrial samples.

The Sb isotope ratio of the drainage water from the Ichinokawa-mine showed an enrichment of the heavy Sb isotope. Because the oxidation state of the Sb dissolved in the water was pentavalent and was most likely $Sb(OH)_6^-$ (Mitsunobu *et al.*, 2006), this fractionation trend is apparently consistent with the heavy isotope enrichment of Sb(V) compared to Sb(III) in stibuite shown in an equilibrium isotopic distribution experiment between Sb(III) and Sb(V) in an aqueous solution (Rouxel et al., 2003). However, the dissolved Sb(III) species released by the dissolution of stibnite (Frederick et al., 2000) is not stable under oxic conditions as it completely transforms into $Sb(OH)_6^-$ in the aqueous phase as seen in the speciation analysis of Sb in the water (Mitsunobu et al., 2006). Because of $Sb(OH)_6^-$ dominance in water and the little reverse reaction to Sb_2S_3 , the epsilon ¹²³Sb value of the initial Sb containing solution is similar to that of the original stibnite. Thus, a more plausible explanation for the isotopic fractionation is that an adsorption equilibrium with Fe hydroxides occurs in the surrounding sediment. This is quite possible since (i) adsorption of Sb onto Fe hydroxides occurs by the formation of an inner-sphere surface complex of Sb (Mitsunobu et al., 2006) and (ii) isotopic fractionation during a sorption reaction can be induced by inner-sphere complexation whereas outersphere complexation may not be accompanied by such isotope fractionation as has been shown for Mo isotopes (Kashiwabara et al., 2009). Our recent experiment of $Sb(OH)_6^-$ adsorption onto ferrihydrite in a laboratory system also indicates a slight enrichment of the heavier isotope for Sb in the aqueous phase compared to adsorbed Sb (Araki et al., 2009). It is suggested that the degree of isotopic fractionation in the drainage water sample is caused by the stepwise adsorption of $Sb(OH)_6^-$ onto Fe hydroxides during the infiltration of Sb containing aqueous solutions into sediments.

CONCLUSIONS

A small Sb isotopic fractionation among ore minerals and chemical reagents was detected using multiple collector ICP-MS. The relative isotopic variation range of 0.05% (Fig. 1) corresponds to the ¹²³Sb/¹²¹Sb isotopic change by 0.00037, which is the change in the isotopic abundance of ¹²¹Sb from 57.207% to 57.219% (from 42.793% to 42.781% for ¹²³Sb) from the currently accepted Sb isotopic abundances of 57.213% and 42.787%, respectively (Chang *et al.*, 1993). The change in Sb atomic weight is then calculated from atomic masses of ¹²¹Sb (120.9038222) and ¹²³Sb (122.9042160) (De Laeter *et al.*, 2003) to be from 121.75986 to 121.75961. This difference in Sb atomic weight by 0.00025 is quite smaller than its currently accepted uncertainty (0.001), as compiled by IUPAC (Loss, 2003). A reduction of the current uncertainty in Sb standard atomic weight may be possible by the improvement in analytical reproducibility reported here.

A slight heavy Sb isotopic enrichment was observed in a drainage water sample from a Sb_2S_3 mine compared to the data from Sb minerals collected in the same area. This enrichment of the heavier isotope of Sb in the aqueous phase compared to the relatively isotopicallyuniform reagents determined by us and that of silicate samples (Rouxel *et al.*, 2003) indicates that Sb input from natural sources has positive or zero epsilon Sb values in aquatic and terrestrial systems. In contrast, anthropogenic Sb input into sediments via air will have a lighter Sb isotope enrichment trend (negative epsilon values) because of evaporation in the smelting process (Weiss *et al.*, 2008). This trend may result in Sb isotopes being a powerful tool for the detection of anthropogenic Sb input into the environment.

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