

Antimony Isotope Ratio Measurements Using a Desolvating Nebulizer System with Multicollector ICP-MS Detection: A Study with an Atlantic Ocean Mn Nodule

Application Note

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Introduction

Hydrogenetic Fe-Mn crusts precipitate directly from seawater and as such have been used as paleoceanographic recorders of changes in seawater chemistry over time.¹ The slow growth rates of Fe-Mn crusts (<10 mm Myr⁻¹)^{1,2} render them ideal archives of long-term variations in marine isotope compositions.^{3,4,5}

Antimony is a redox sensitive element (with two oxidation states under terrestrial conditions, Sb³⁺ and Sb⁵⁺), that may be sensitive to past environmental conditions. The 35 kyr residence⁶ time of Sb in the oceans is long compared to that of ocean overturning times (1.5 kyrs)^{7,8}; therefore, Sb should be uniform in the oceans. Differences in the Sb isotopic composition could reflect numerous changes in inputs and outputs of the Earth's past environment such as hydrothermal inputs⁹, rate of marine organic burial¹⁰ and weathering¹¹. Antimony isotope fractionation can arise during adsorption¹², with the magnitude of fractionation temperature dependent. Therefore, the change in ocean temperatures during the Cenozoic Era¹³ could also result in variations in the Sb isotope composition.

Modern day variations of Sb isotopes on the Earth's surface show $((^{123}\text{Sb}/^{121}\text{Sb})_{\text{samp}} / (^{123}\text{Sb}/^{121}\text{Sb})_{\text{std}})^{-1} < 0.5\text{‰}$ variations¹⁴, so a high level of measurement precision is needed to investigate these past processes. This requirement is achieved using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) with a specialized desolvating nebulizer accessory for signal enhancement. A second obstacle to overcome is the efficient removal of Te, which has an isobaric interference on ¹²³Sb. To prove the validity of the method, we investigate another deep marine sedimentary deposit, the USGS reference sample manganese nodule Nod-A-1, which is chemically similar to FeMn crusts.

Instrumentation

The MC-ICP-MS instrument used was a Nu Instruments Sapphire setup in high-energy mode. The desolvating nebulizer accessory coupled to the Sapphire was the Aridus 3 (Teledyne CETAC Technologies); liquid samples were introduced via a self-aspirating concentric PFA nebulizer (Elemental Scientific PFA-100 type, 100 $\mu\text{L}/\text{min}$) connected to the heated PFA spray chamber of the Aridus 3.

A front view of the Aridus 3 is depicted in Figure 1. The PFA nebulizer and PFA spray chamber are on the left front side of the Aridus 3, behind a transparent door. Argon gas flow to the PFA nebulizer is supplied from the host Sapphire MC-ICP-MS and is controlled by the Sapphire software.

The Aridus 3 was placed on the benchtop near the Sapphire MC-ICP-MS, as shown in Figure 2. A sample transfer tube assembly was connected between the outlet of the Aridus 3 and the MC-ICP-MS torch.

An argon sweep gas supply and a nitrogen addition gas supply were connected to the back panel of the Aridus 3; both gas flows were set using dedicated mass flow controllers that are integrated into the Aridus 3. An Aridus 3 computer software program (AridusLink) enabled adjustment of these two gas flows as well as the temperature settings of the PFA spray chamber and the membrane desolvator oven module. A schematic of the Aridus 3 gas flows is shown in Figure 3.

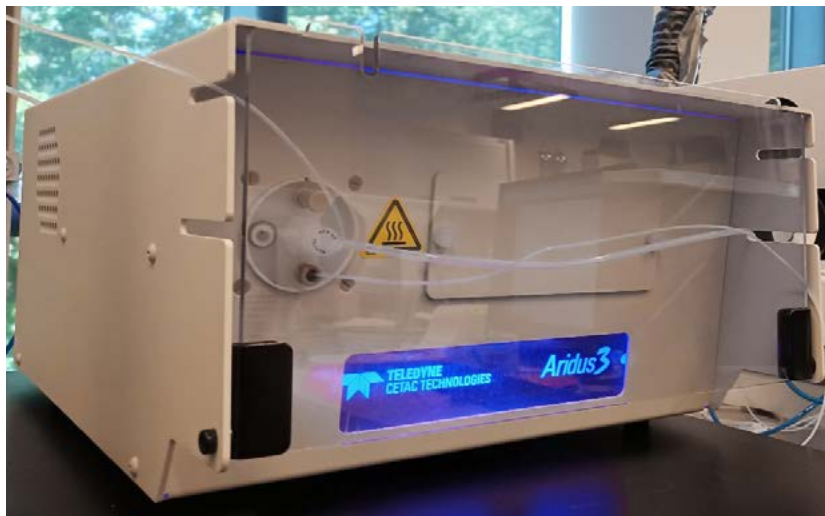


Figure 1. Aridus 3 Front View at Ready Status (blue color status light)

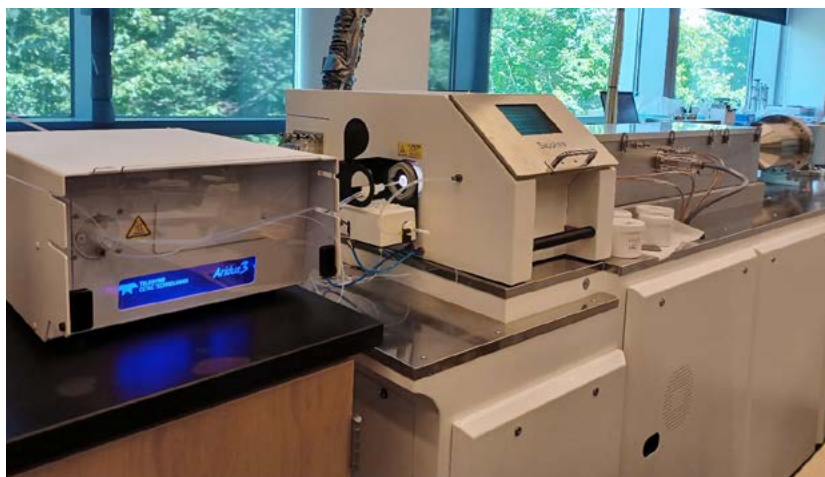


Figure 2. Nu Instruments Sapphire MC-ICP-MS with Aridus 3 Desolvating Nebulizer Accessory

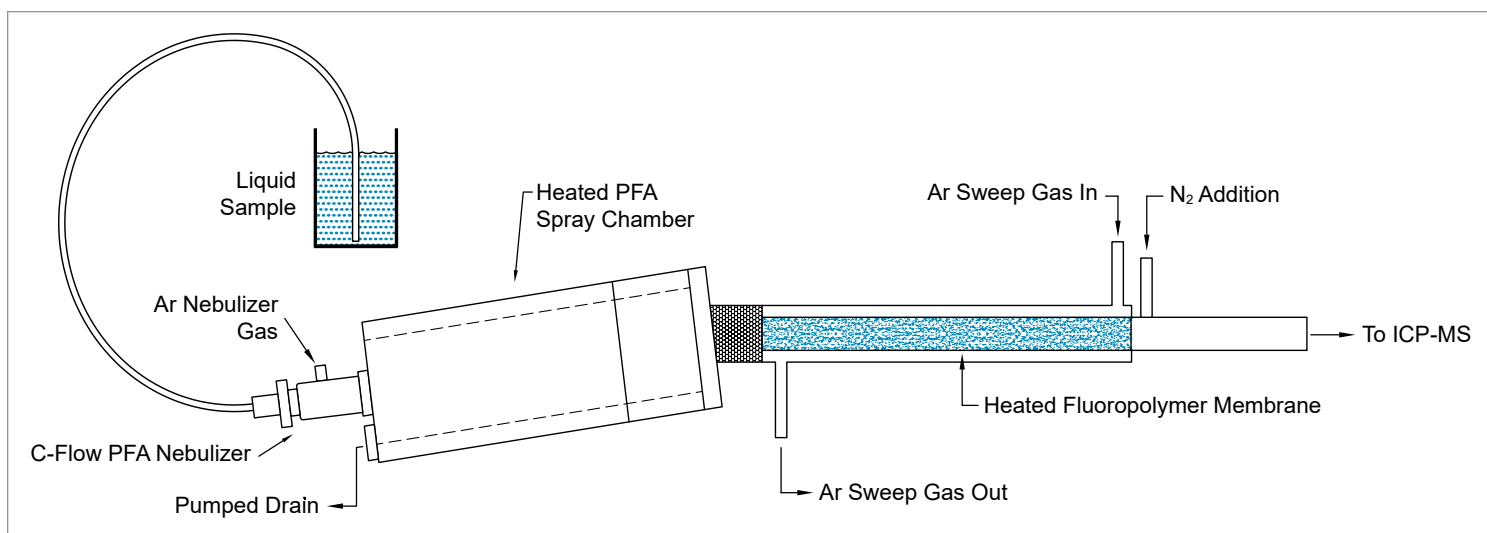


Figure 3. Aridus 3 Schematic with Gas Flows

Operating Conditions

Operating conditions for the MC-ICP-MS are given in Table 1, including details for data acquisition and tuned sensitivity. The AridusLink control screen with Aridus 3 temperature and gas flow settings is depicted in Figure 4. Note that no N₂ addition gas flow was used in experiments with the Nu Instruments Sapphire ICP-MS.

Sample Description

United States Geological Survey (USGS) Nod-A-1 is a homogenized manganese nodule prepared in the early 1980s as a geological reference standard. The sample was taken along the Blake Plateau (western Atlantic Ocean off the southeastern USA coast) at a depth of 788 meters.

Sample Preparation

An approximately 0.1 g sample of USGS Nod-A-1 was dissolved using 2 mL 6M HCl and 0.5 mL 15M HNO₃ in a 7-mL PFA vial at temperatures not exceeding 80 °C. To test for complete dissolution and to ensure that no volatile species of Sb were lost, replicates were taken which reproduced the same Sb concentration and isotopic composition. Purification of the samples followed the column chemistry method from Liu et al (2020)¹⁵ which resulted in the removal of >95% of Te and signals of ¹²³Sb 2000x greater than ¹²³Te. Replicate samples were diluted to a final volume of 20 mL and an Sb concentration of 20 µg/L using 2% nitric acid.

Instrument Operating Conditions

Table 1. Nu Instruments Sapphire MC-ICP-MS

Parameter	Value
RF Power	1200 W
Coolant Gas	14 L/min
Auxiliary Gas	1.21 L/min
Sample Gas	1.03 L/min
Extraction Voltage	3759.0 V
Sampler and Skimmer	Nickel
Quad 1	-25.2 V
Quad 2	168.2 V
Resolution	Low
Measured Liquid Uptake	0.08 ml/min
Liquid Sample Matrix	2% HNO ₃
Block Length	50x measurements with 3 sec integrations
Typical Block Uncertainty	2σ, 1x10 ⁻⁵
Tuned Sensitivity	20ppb of Sb resulted in total signal of 7.5 V.

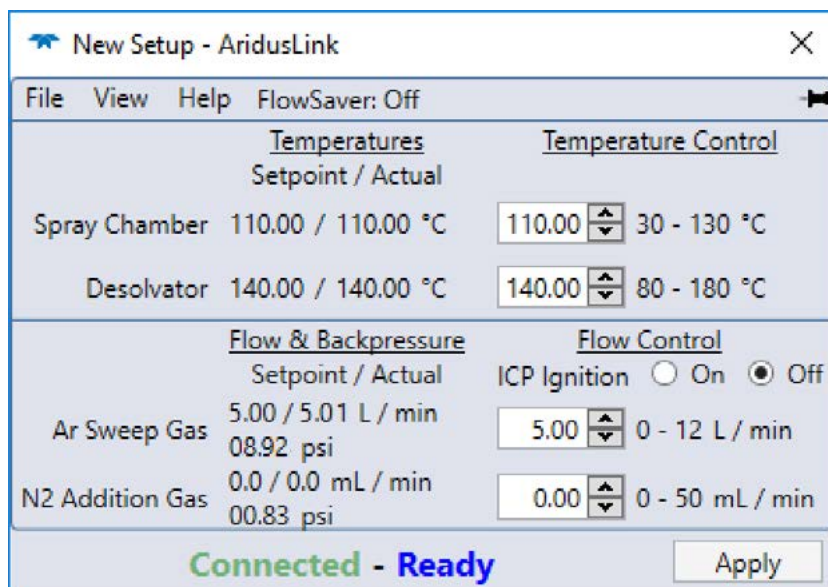


Figure 4. AridusLink Software Control Screen of System Temperatures and Gas Flows

Tellurium Correction

Tellurium-doped standards were run to demonstrate the effect of the Te correction on the $^{123}\text{Sb}/^{121}\text{Sb}$ ratio. Solutions of 20 $\mu\text{g}/\text{L}$ Sb prepared from National Institute of Standards and Technology (NIST) Sb Standard Solution 3102a were mixed with 2, 5, 10 and 20 $\mu\text{g}/\text{L}$ of Te and analyzed. ^{125}Te was also measured to monitor the Te signal. Undoped 20 $\mu\text{g}/\text{L}$ Sb was used for sample standard bracketing. Table 2 shows that the uncorrected values produce significant deviations (units of ‰) from the reference standard value; Figure 5 depicts these results graphically.

An iterative Te correction was applied. The natural $^{125}\text{Te}/^{123}\text{Te}$ ratio was corrected for the machine fractionation, as recorded in the $^{123}\text{Sb}/^{121}\text{Sb}$ ratio. The $^{123}\text{Sb}/^{121}\text{Sb}$ ratio was then corrected for Te interference, with the process repeated until the Sb ratio converged. This occurred in one to two iterations. The corrected values were within error of the reference standard for all Te:Sb ratios; Te:Sb ratios in this test were far greater than that for natural samples prepared using the column chemistry described above.

Table 2. $^{123}\text{Sb}/^{121}\text{Sb}$ ratios corrected for Te interferences.

Te ($\mu\text{g}/\text{L}$)	$\delta^{123}\text{Sb}_-$		$\delta^{123}\text{Sb}_-$	
	uncorrected (‰)	2 σ	corrected (‰)	2 σ
2	2.08	0.10	-0.01	0.11
5	4.86	0.07	-0.05	0.05
10	9.45	0.11	0.00	0.07
20	19.84	0.11	0.02	0.09

Results

Sample standard bracketing was used to correct for machine fractionation, with NIST Sb Standard Solution 3102a used as the bracketing standard.

The ratio is presented in the delta notation for $^{123}\text{Sb}/^{121}\text{Sb}$ in parts per thousand, normalized to NIST 3102a. The $\delta^{123}\text{Sb}$ value of the Nod-A-1 was stable over the 8+ hour run. The average $\delta^{123}\text{Sb}$ value of the Nod-A-1 was 0.29‰ and the 2 standard deviation reproducibility is 42 parts per million.

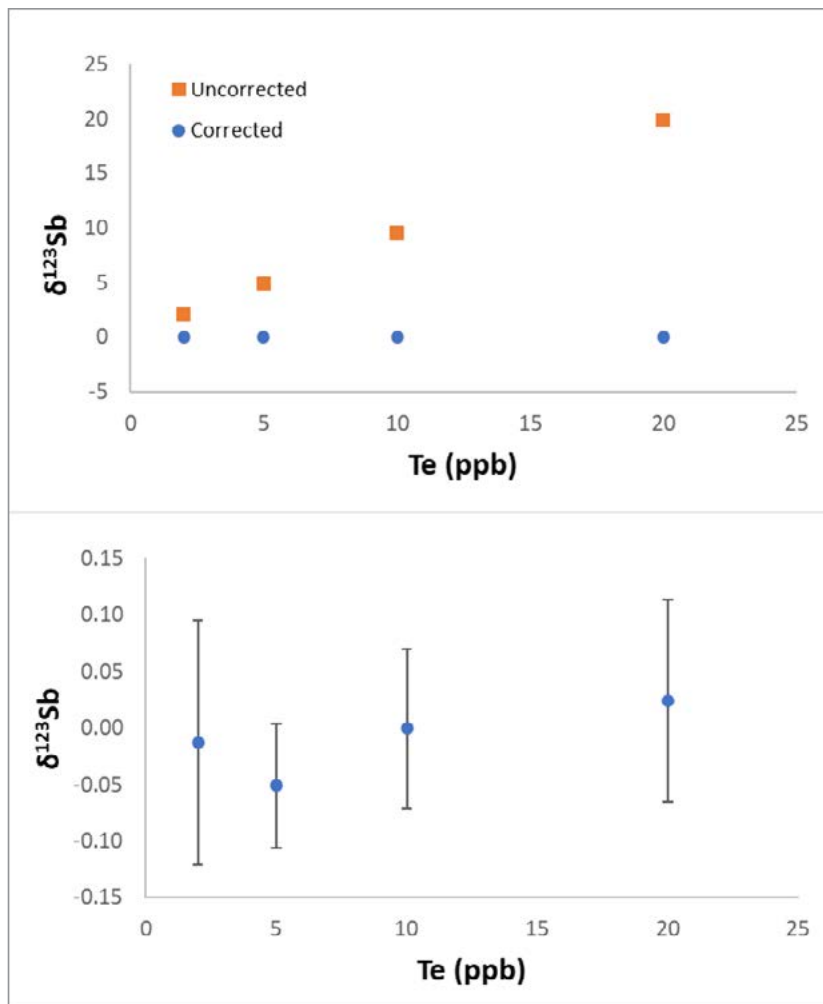


Figure 5. Te uncorrected and corrected $\delta^{123}\text{Sb}$ values. a. shows the uncorrected and corrected values, 2 std error bars are 0.11‰ or less. b. only corrected values which are within error of the reference standard at all Te concentrations.

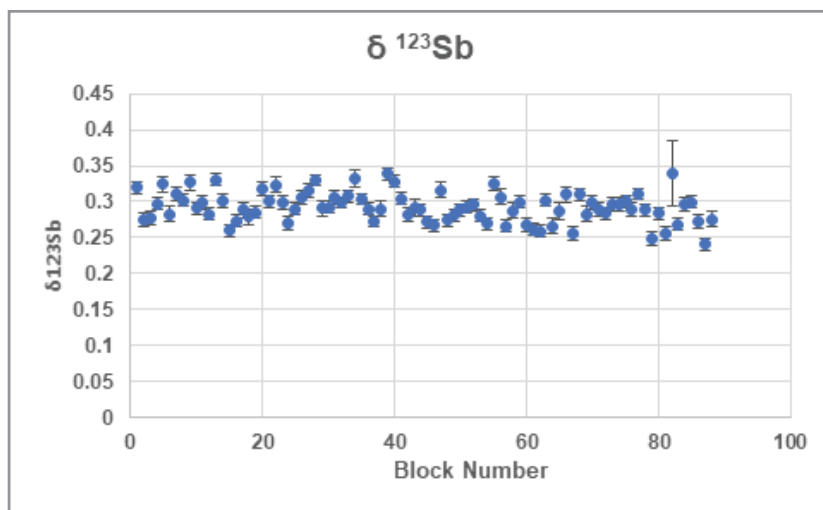


Figure 6. $\delta^{123}\text{Sb}$ values of USGS reference sample Nod-A-1 measured over an 8-hour session

Conclusions and Summary

Consistent measurement behavior of Te allows for accurate corrections of isobaric ^{123}Te on the ^{123}Sb signal. Combined with the preconditioning method of Liu et al. (2020)¹⁵, the high Te concentrations in sedimentary marine deposits do not present a barrier to high precision Sb isotope measurements. A reproducibility of 42ppm for measurements of marine sedimentary deposits is possible using multicollector ICP-MS with an Aridus 3 desolvating nebulizer accessory, allowing investigations into the record of past climate contained within these samples.

Acknowledgements

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References

1. Hein J.R., Koschinsky A., Halbach P., Manheim F.T., Bau M., Kang J-K., and Lubick N. *Geol. Soc. Spec. Publ.*, 1997, **119**, 123.
2. Henderson G.M. and Burton K.W. *Earth Planet Sci. Lett.*, 1999, **170(3)**, 169.
3. Burton K.W., Ling H.F. and O'Nions R.K. *Nature*, 1997, **386(6623)**, 382.
4. Christensen J.N., Halliday A.N., Godfrey L.V., Hein J.R. and Rea D.K. *Science*, 1997, **277(5328)**, 913.
5. Zhu, X. K., O'Nions R.K., Guo Y. and Reynolds B.C. *Science*, 2000, **287(5460)**, 2000.
6. Hem J.D. *Study and Interpretation of the Chemical Characteristics of Natural Water*. 1985, US Geological Survey, Reston, VA.
7. Broecker, W.S. and Peng, T.H., 1982. *Tracers in the Sea*. 1982, Eldigio Press, Palisades, NY.
8. Elderfield, H. and Greaves, M.J. *Nature*, 1982, **296**, 214.
9. Gall L., Williams H.M., Siebert C., Halliday A.N., Herrington R.J., and Hein J.R. *Earth Planet Sci. Lett.*, 2013, **375**, 148.
10. Nielsen S.G., Mar-Gerrison S., Gannoun A., LaRowe D., Klemm V., Halliday A.N., Burton K.W. and Hein J.R. *Earth Planet Sci. Lett.*, 2009, **278**, 297.
11. David K., Frank M., O'Nions R.K., Belshaw N.S and Arden J.W. *Chem. Geol.*, 2001, **178**, 23.
12. Zhou W., Zhou A., Wen B., Liu P., Zhu Z., Finfrock Z. and Zhou J. *J. Hazard. Mater.* 2022, **429**, 128317.
13. Zachos J., Pagani M., Sloan L., Thomas E. and Billups K. *Science*, 2001, **292**, 686.
14. Sun G., Wu Y., Feng X., Wu X., Li X., Deng Q., Wang F. and Fu X. *Chem. Geol.*, 2021, **582**, 120459.
15. Liu, J., Chen J., Zhang T., Wang Y., Yuan W., Lang Y., Tu C., Liu L. and Brick J.-L. *J. Anal. At. Spectrom.*, 2020, **35**, 1360.

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