Isotope Ratio Measurements for Sample Dating Studies Using Multicollector ICP-MS and Signal Enhancement via a Desolvating Nebulizer Accessory with Nitrogen Gas Addition

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Abstract

Multicollector ICP-MS instruments are widely used in geochemistry for high precision isotope ratio measurements. Isotope signal enhancement and/or mass spectral interference reduction (ex. oxides and hydrides from any injected water) is often necessary for useful measurement of low abundant isotopes and mass-limited samples.

This work will describe the setup, optimization, and use of an advanced desolvating nebulizer accessory for multicollector ICP-MS. Important accessory benefits include a low flow self-aspirating concentric nebulizer with inert liquid flow path, a heated inert spray chamber and membrane desolvator with adjustable temperatures for optimum sample transport efficiency, and dedicated mass flow controllers with computer software control for Ar sweep and N_2 addition gases for ease of tuning in the host multicollector ICP-MS software.

The desolvating nebulizer accessory is especially applicable with multicollector ICP-MS analyses for uranium-thorium dating, as is commonly used for dating travertine, speleothem, marine coral calcite and aragonite samples. System setup parameters and dating measurements will be presented for representative sample types.

Instrumentation - I

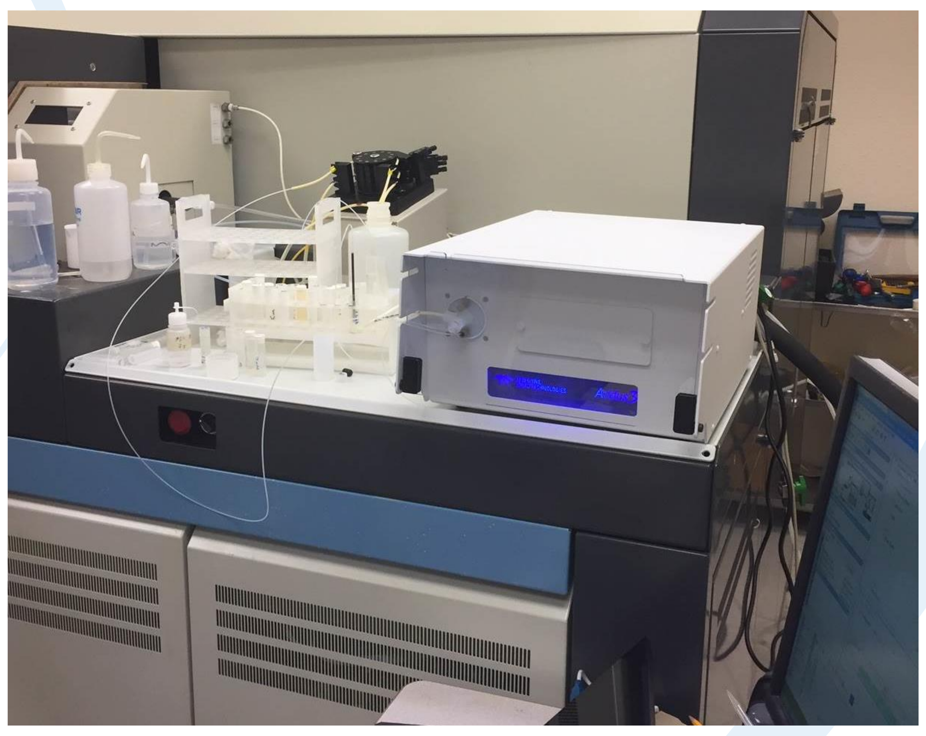


Fig 1. Thermo Fisher Neptune MC-ICP-MS w. Aridus3

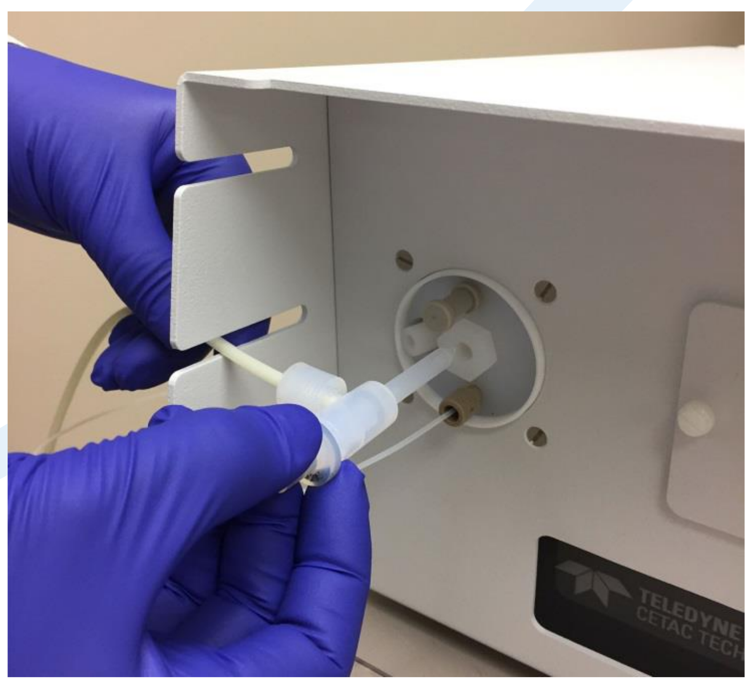


Fig 2. CFlow-100 PFA Nebulizer w. Aridus3 PFA Spray Chamber

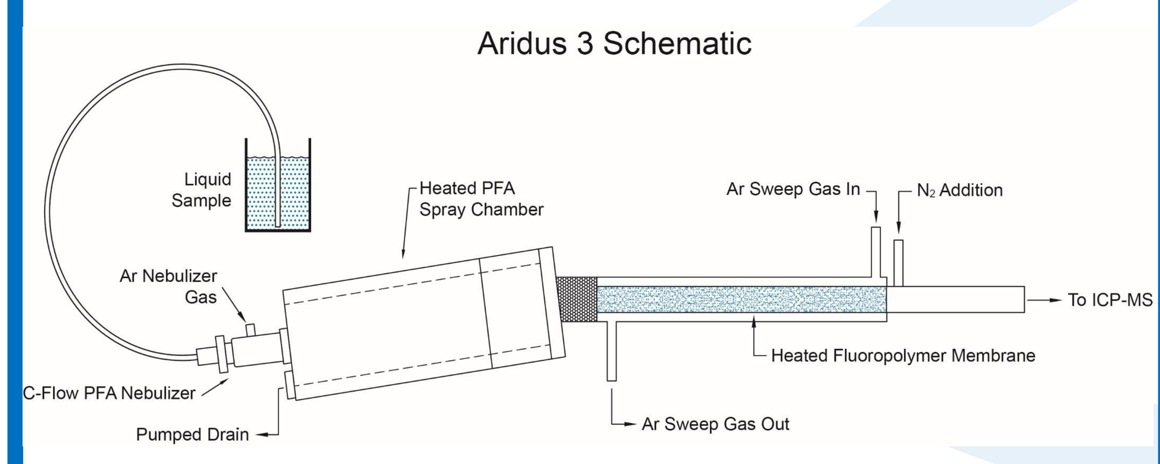


Figure 3. Aridus3 Schematic w. Gas Flows

Operating Conditions

Thermo Neptune MC-ICP-MS

ICP Power	1200 W
Coolant Gas	15.00 L/min
Auxiliary Gas	0.77 L/min
Sample Gas	0.968 L/min
Interface	Jet Type
Extraction	-2000 V
Focus	-626.0 V
X-Defl.	8.46 V
Y-Defl.	0.02 V
Shape	193.00 V
Rot Quad 1	0.01 V
Source Offset	-10.00 V
Resolution	Low
Guard Electrode	On
Jet Interface	Cones Only

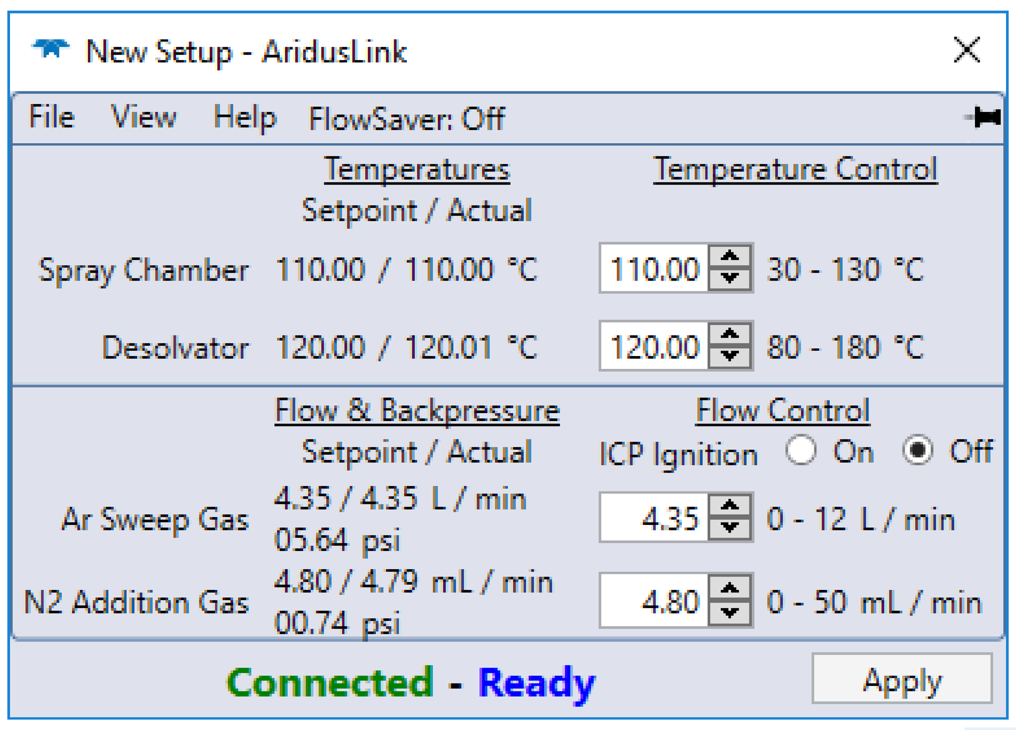


Figure 4. Aridus3 Software Control Screen of System Temperatures & Gas Flows

Sample Types and Preparation

A. In-house standard having no detrital Th and high U concentration
B. In-house standard having no detrital Th and low U concentration
C. Submerged stalagmite; checking age and U and Th concentrations
D. Altered stalagmite; checking its age and U and Th concentrations
E. Stalactite; checking the antiquity of the sample

U-Series Methods: Summary

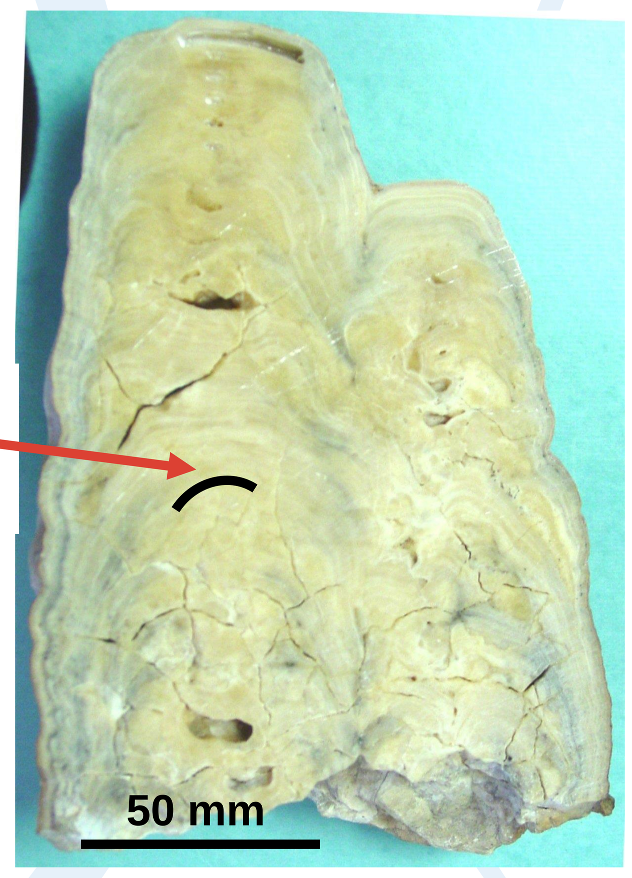
Subsample powders were milled from samples C, D, and E in areas that looked cleanest of detritus. Powders generally 20 to 100 mg in mass were dissolved in 15N HNO_3 and spiked with a mixed ^{229}Th-^{233}U-^{236}U solution. Subsamples were then dried and re-dissolved in 7N HNO_3 and added to anionic resin columns to separate the U and Th. Spiked aliquots of U and Th in 3% HNO_3 solution were analyzed using the Thermo Neptune MC-ICP-MS with the Aridus3. Results were reduced to obtain sample dates using the procedures reported by Cheng et al. (see below).

Cheng, H., Edwards, R.L., Shen, C.-C., Polyak, V.J., Asmerom, Y., Woodhead J., Hellstrom, J., Wang, Y., Kong, X., and Spötl, C., Improvements in ^{230}Th dating, ^{230}Th and ^{234}U half-life values, and U-Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry, Earth and Planetary Science Letters, v. 371, p.82-91, 2013.

Sample Pictures

Fig. 5 Sample D: Altered Stalagmite, Hidden Cave, Guadalupe Mountains, NM

Testing age of altered layers: 22,960 ± 1500 BP



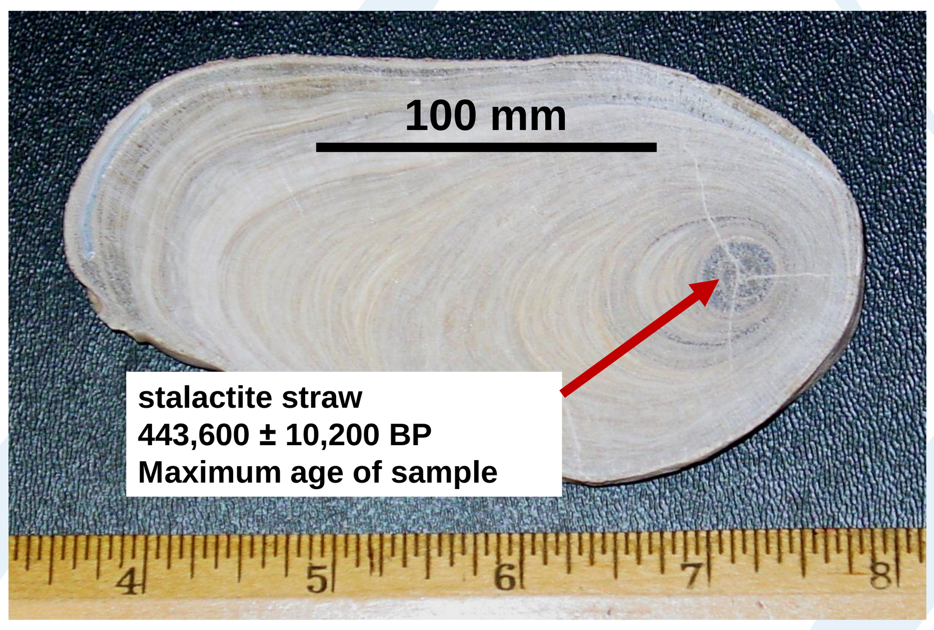


Figure 6. Sample E : Old Stalagmite (cross-section) Fort Stanton Cave, Central New Mexico

Table 1a. Sample Results

Sample	U (ppb)	Th (ppt)	^{230}Th/^{232}Th	^{230}Th/^{238}U
A	3395.0 ± 2.2	2 ± 2	1777371 ± 1526049	0.302 ± 0.001
B	140.3 ± 0.1	5 ± 0	13538 ± 1095	0.143 ± 0.000
C	998.8 ± 1.1	4103 ± 31	359.24 ± 2.88	0.483 ± 0.001
D	105.6 ± 0.1	11615 ± 13	14.65 ± 0.07	0.527 ± 0.003
E	832.0 ± 0.4	12528 ± 8	312.20 ± 0.67	1.538 ± 0.003

Table 1b. Sample Results

Sample	δ^{234}U(‰)m	δ^{234}U (‰)i	Age Uncorrected (years BP)	Age Corrected (years BP)
A	15 ± 1	17 ± 1	38518 ± 109	38516 ± 109
B	473 ± 1	488 ± 2	11088 ± 42	11035 ± 50
C	72 ± 1	86 ± 2	64765 ± 274	64349 ± 343
D	1437 ± 3	1533 ± 7	25952 ± 151	22959 ± 1496
E	409 ± 1	1429 ± 42	443996 ± 10235	443587 ± 10204

All ratios are activity ratios. Errors are absolute 2σ.
m = measured value i = initial value BP = before present

Notes and Summary

Using the Teledyne CETAC Aridus3 desolvating nebulizer enhances the signal by a factor of 4 to 5 making analyses easier and quicker. Note that the Neptune MC-ICP-MS was equipped with Jet sample and X interface skimmer cones but not with the high performance interface vacuum pump. Smaller samples can be analyzed, which can also reduce sample column chemistry time.

Reference on N_2 Addition

G.L Scheffler and D. Pozebon, Advantages, drawbacks, and applications of mixed Ar-N_2 sources in inductively coupled plasma – based techniques: an overview, Anal. Methods, 2014, 6, 6170-6182.

Acknowledgement

We would like to thank Dr. Yemane Asmerom of the University of New Mexico EPS for his assistance with tests of the Teledyne CETAC Aridus3 unit with the Thermo Neptune MC-ICP-MS.

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