

# Multicollector ICP-MS with a Desolvating Nebulizer System for U-Series Dating of Late Pleistocene Terrestrial Snails

Fred G. Smith, Teledyne CETAC Technologies

14306 Industrial Road, Omaha, NE 68144-3334 USA [Fred.Smith@Teledyne.com](mailto:Fred.Smith@Teledyne.com)

Yemane Asmerom and Victor Polyak, University of New Mexico, Department of Earth and Planetary Sciences, Albuquerque, NM 87131 USA [asmerom@unm.edu](mailto:asmerom@unm.edu) [Polyak@unm.edu](mailto:Polyak@unm.edu)

## Abstract

Multicollector ICP-MS instruments are very specialized devices for high precision isotope ratio measurements. For useful measurement of low abundant isotopes and mass-limited samples, signal enhancement is often required. In addition, sample preparation and/or sample aerosol desolvation may be necessary to reduce or eliminate mass spectral interferences such as oxides and hydrides.

This poster will examine the application of MC-ICP-MS with a desolvating nebulizer accessory for U-series dating of late Pleistocene terrestrial snails (gastropods). Experimental details such as sample preparation steps, MC-ICP-MS operating conditions, and desolvating nebulizer gas flows (Ar sweep gas and N<sub>2</sub> addition gas) will be presented.

The MC-ICP-MS signal enhancement provided via a desolvating nebulizer system enables the use of less sample (1 to 10 mg) for dating measurements. For terrestrial gastropods to be used in paleoclimate or archaeological studies, absolute errors on ages must be accurate and well constrained. Our first results show that, for aragonitic samples, there is enough U to produce meaningful ages with small absolute errors. For example, NM-Gstro-1, having a U concentration of 2.6 ppm, yielded an age of 23,344 ± 107 years before present from only 6 mg of sample. The desolvating nebulizer system makes these measurements routinely possible.

## Sample Preparation / Introduction

Sub-samples were dissolved in 15 N HNO<sub>3</sub>, then spiked with a mixture of <sup>229</sup>Th, <sup>233</sup>U, and <sup>236</sup>U and fluxed at moderate heat for one hour. U and Th were separated using Eichrom 1x8, 200-400 mesh chloride-form anion exchange resin. All samples were analyzed on a Thermo Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) using a Teledyne CETAC Aridus II Desolvating Nebulizer System. Standards NBL-112 (U) and an in-house <sup>230</sup>Th-<sup>229</sup>Th solution were analyzed several times during the run sessions. More accurate radioactive half-lives for <sup>230</sup>Th and <sup>234</sup>U and improved MC-ICP-MS analytical methods were used in this study (Cheng et al. 2013).

## Reference

H. Cheng, R.L. Edwards, C.-C. Shen, V. J. Polyak, Y. Asmerom, J. Woodhead, J. Hellstrom, Y. Wang, X. Kong, C. Spotl, X. Wang, E. Calvin Alexander Jr., Improvements in <sup>230</sup>Th Dating, <sup>230</sup>Th and <sup>234</sup>U Half-Life Values, and U-Th Isotopic Measurements by Multi-collector Inductively Coupled Plasma Mass Spectrometry, Earth Planet. Sci. Lett. 371-372, 82-91 (2013).

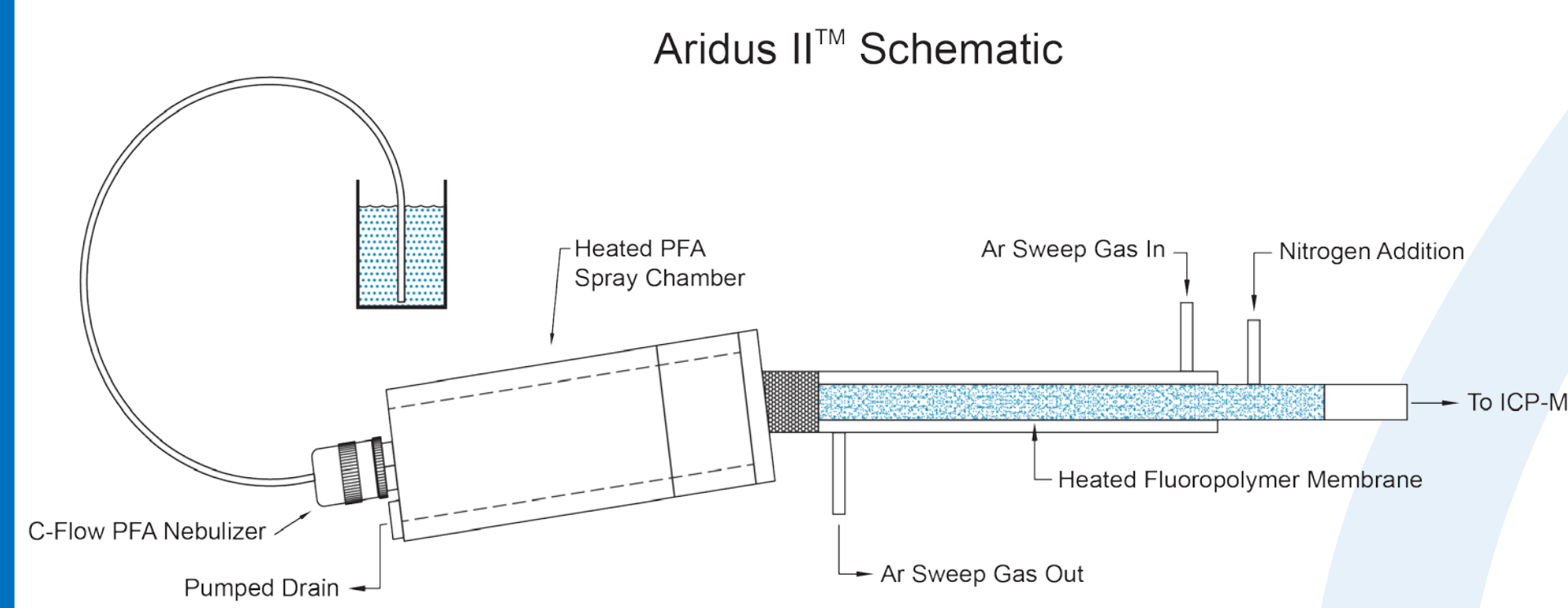
## Instrumentation



Figure 1. Thermo Neptune MC-ICP-MS with CETAC Aridus II Desolvating Nebulizer System



Figure 2. Aridus II Desolvating Nebulizer System



## Operating Conditions

### Thermo Neptune MC-ICP-MS Conditions:

ICP Power	1200 W
Coolant Gas	15 L/min
Auxiliary Gas	0.9 L/min
Sample Gas	1.0 L/min
Interface	Jet Type

### CETAC AridusII Conditions:

PFA Nebulizer	C-Flow 100
Uptake Rate	100 µL/min
Spray Chamber Temp	105°C
Membrane Oven Temp	160°C
Ar Sweep Gas	9.0 L/min
N <sub>2</sub> Addition Gas	5 mL/min

## Samples of Terrestrial Gastropods

Tx-Gstro are two samples of the Pupillidae family, possibly *Pupilla muscorum* from a road cut in Gaines County, Texas.

NM-Gstro are samples of Succineidae family from a shallow road cut in Lea County, New Mexico, near Bronco, Texas.

These samples are typical of Late Pleistocene terrestrial gastropods in this region.

## Gastropod Sample Images



Figure 4a. Tx-Gstro-1



Figure 4b. Tx-Gstro-2



Figure 5a. NM-Gstro-2

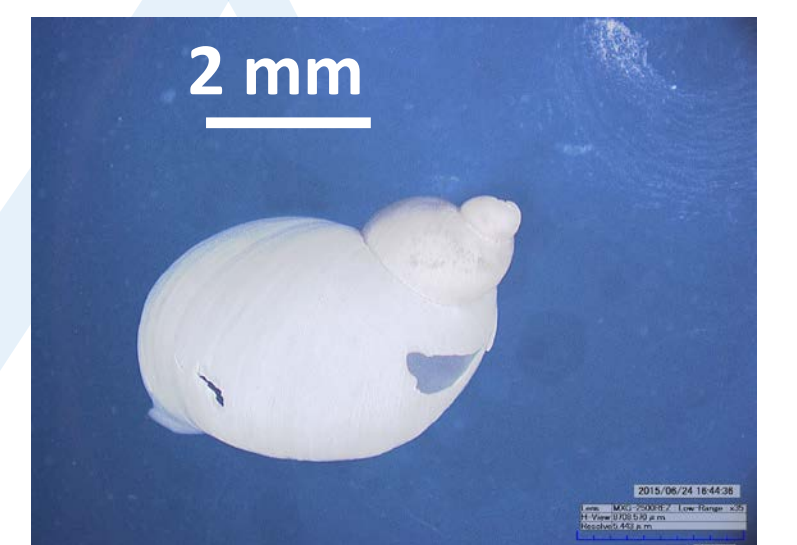


Figure 5b. NM-Gstro-4

Table 1. U-Series Results for Terrestrial Gastropod Samples

Sub-sample	<sup>238</sup> U (ppb)	<sup>232</sup> Th (ppt)	<sup>230</sup> Th/ <sup>232</sup> Th activity	<sup>230</sup> Th/ <sup>238</sup> U activity
Tx-Gstro-1	454.10 ± 4.56	515071 ± 13140	2.14 ± 0.09	0.7930 ± 0.0276
Tx-Gstro-2	151.47 ± 0.57	139525 ± 1915	2.46 ± 0.07	0.7408 ± 0.0196
NM-Gstro-1	2559.51 ± 1.87	24456 ± 77	98.03 ± 0.37	0.3065 ± 0.0007
NM-Gstro-2	1650.28 ± 1.91	110235 ± 422	19.54 ± 0.09	0.4272 ± 0.0012
NM-Gstro-3	1667.18 ± 1.70	579433 ± 877	4.21 ± 0.01	0.4792 ± 0.0013
NM-Gstro-4	1131.99 ± 2.31	439961 ± 1654	4.04 ± 0.02	0.5139 ± 0.0026

Sub-sample	δ <sup>234</sup> U <sub>meas</sub> ‰	δ <sup>234</sup> U <sub>initial</sub> ‰	Age Uncorr (yrs BP)	Age Corrected (yrs BP)
Tx-Gstro-1	511 ± 5	596 ± 20	77125 ± 3819	54490 ± 11301
Tx-Gstro-2	543 ± 5	626 ± 17	68202 ± 2452	50515 ± 8811
NM-Gstro-1	561 ± 2	599 ± 2	23518 ± 62	23344 ± 107
NM-Gstro-2	585 ± 2	641 ± 2	33568 ± 114	32378 ± 604
NM-Gstro-3	560 ± 2	614 ± 6	39098 ± 133	32668 ± 3175
NM-Gstro-4	541 ± 2	598 ± 7	43140 ± 276	35851 ± 3600

## Notes

All errors are reported as absolute 2σ. Correction of ages was based on <sup>230</sup>Th/<sup>232</sup>Th atomic ratio = 4.4 × 10<sup>6</sup> ± 50%. Sub-sample masses analyzed are Tx-Gstro-1 = 1.03 mg, Tx-Gstro-2 = 4.25 mg, NM-Gstro-1 = 6.12 mg, NM-Gstro-2 = 12.82 mg, NM-Gstro-3 = 12.59 mg, NM-Gstro-4 = 5.66 mg.

## Summary

MC-ICP-MS coupled with a desolvating nebulizer system allows a lower range of gastropod sample masses (1.03 mg to 12.82 mg) to be used, preserving valuable sample and reducing sample preparation reagent usage.