# Determination of initial $^{230}Th/^{232}Th$ ratios in a speleothem from Spring Valley Caverns, Minnesota, using fluorescent annual banding


Dasgupta, Sushmita,[1] Edwards, R. Lawrence,[1] Shen, Chuan-Chou,[2] Alexander, Jr., E. Calvin[1]

(1) Department of Geology and Geophysics, University of Minnesota, 310 Pillsbury Dr SE, Minneapolis, MN 55455 USA

(2) Department of Geosciences, National Taiwan University, Taipei, Taiwan 106, R.O.C.


## Motivation:

$^{230}Th$ dating is a widely used technique for reconstructing high-resolution chronology of paleoclimate data from speleothems (e.g. Richards & Dorale, 2003, Reviews in Mineralogy and Geochemistry 52, 407). The accuracy of the calculated ages is constrained by the variability of initial $^{230}Th/^{232}Th$ ratio in the sample, especially for Holocene speleothems with high detrital $^{232}Th$ contents. In order to accurately determine the initial $^{230}Th/^{232}Th$ ratio an independent measure of age is required. Annual banding is one such independent chronometer.

Stalagmite samples collected from Spring Valley Caverns, Minnesota showed substantial variability in $^{232}Th$ concentration in several sub-layers with significant uncertainty in the calculated ages. The samples also contained fluorescent banding due to the presence of organic matter in them. Using opaque detrital layers in the sample as markers we were able to show that the banding pattern replicated in coeval stalagmites.

In this study we investigate the annual nature of banding and explored the use of these fluorescent annual bands to estimate the initial $^{230}Th/^{232}Th$ ratios over the last 1000 years in a stalagmite with variable $^{232}Th$ contents ($10^{-12}$ to $10^{-9}$ g/g).

## Methods:

Dating

- U-series disequilibrium dating method was employed.
- U and Th were measured by Element 1, a single collector ICP-MS at the Minnesota Isotope Lab following the technique of Shen et al. 2002 (Chemical Geology 185, 165-178)
- U concentration ranged from 2.5 – 3 ppm.
- Average sample size used was 100 mg.

Imaging

Speleothems fluoresce due to the presence of organic matter, such as humic and fulvic acids, in them. This fluorescence is observed by exciting the organics in the sample with high energy light.

- Samples SVC982 and SVC983-1 were imaged with a laser scanning confocal microscope BioRad MRC 1024.
- The wavelength of excitation was 488 nm and emission filter used was 522 nm.
- Images were processed and stitched together using Adobe Photoshop.
- The bands are characterized by light or fluorescing part and dark and non fluorescing part.
- The lighter bands were counted to obtain an age.

## *Experiment 1*

- Compared fluorescent banding between two samples.
- $^{230}Th$ dates with low concentration of $^{232}Th$ were selected for SVC983-1.
- Bands were constrained with a precise $^{230}Th$ date and counted downward from this date.
- Band counted ages were compared with $^{230}Th$ ages.

### Polished sample and fluorescent image

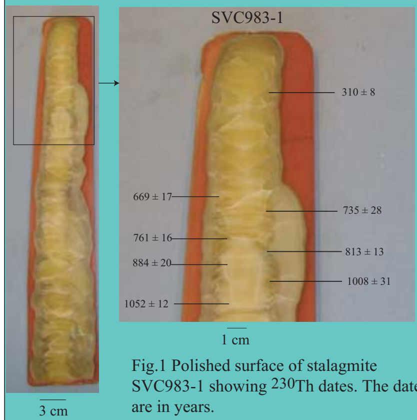



Fig.1 Polished surface of stalagmite SVC983-1 showing $^{230}Th$ dates. The dates are in years.

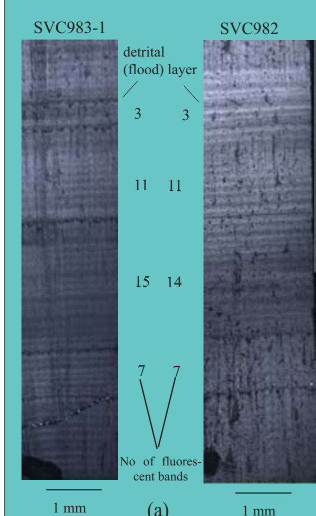

Fig. 2 Image of fluorescent bands from SVC983-1. The lighter bands are the fluorescing part and the darker, the non fluorescing part. Bands were counted assuming the couplets together make up a year.

### Polished sample and fluorescent image


Fig.3 Polished surface of stalagmite SVC982 showing $^{230}Th$ dates in years.


Fig.4 Image of stalagmite SVC982 showing fluorescent bands.

### Comparison of flood bands and fluorescent bands



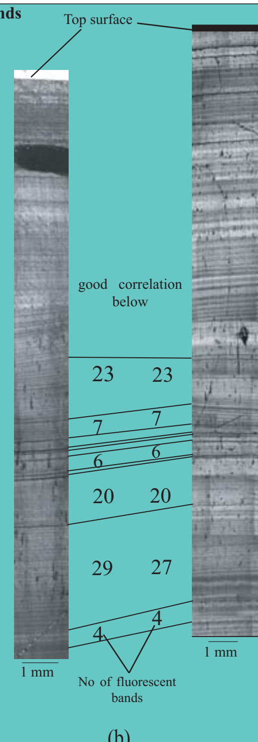




Fig. 5 Comparison of banding between SVC983-1 and SVC982. The dark layers are flood bands, composed of detrital minerals. These were used as markers

a) Good correlation between 3 cm and 4 cm depths

b) From top till 10.2 mm depth for SVC982 and till 8 mm depth for SVC983-1 banding do not match. But good correlation between the samples is observed below these depths.

### Comparison of $^{230}Th$ dates and band counts

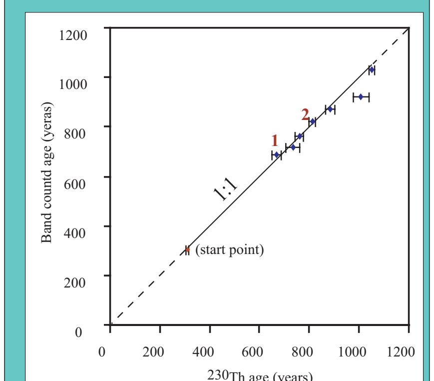


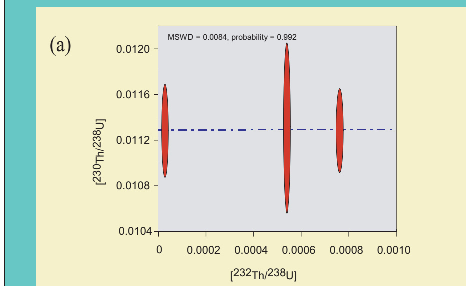

Fig. 6 Plot of band counted age against $^{230}Th$ age for SVC983-1. The red data point marks the $^{230}Th$ age used to constrain the band ages. The diagonal line marks 1:1 relationship between the band counted age and the $^{230}Th$ age and is not a regression line. Within error the band counted age matches the $^{230}Th$ age, demonstrating the annual nature of banding.

The dates marked 1 & 2 are used in Experiment 2 to estimate initial $^{230}Th/^{232}Th$ ratios.

## *Experiment 2*

- Selected two layers
- Estimated initial $^{230}Th/^{232}Th$ ratios for the selected layers from band counting
- Performed isochron analyses for these layers. Drilled 3 to 4 subsamples along one layer and obtained individual dates for them.

### Isochron Plots



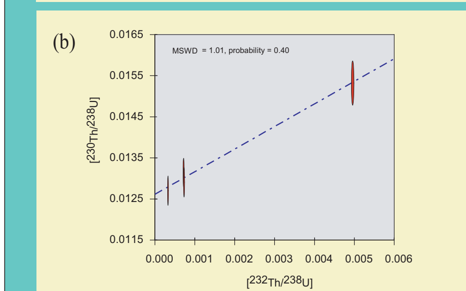




Fig. 7. Plots of 3D isochron analyses of dates 1 (a) and 2 (b). All the ratios are activity ratios (No of atoms x decay constant). The error ellipses are 2 sigma uncertainties.

Table 1: Comparison of initial $^{230}Th/^{232}Th$ predicted from band counting and determined from isochron method. The estimated error on band counting is 3% obtained from missing band between samples.

| Date | Band age | Initial Predicted from band age ($x 10^{-6}$) | Isochron age | Initial from isochron analysis ($x 10^{-6}$) |
|---|---|---|---|---|
| 1 | 763 ± 23 | 2.8 ± 2.0 | 771 ± 22 | 0.1 ± 6.0 |
| 2 | 871 ± 26 | 5.0 ± 1.9 | 877 ± 13 | 3.0 ± 0.6 |

## Discussion:

We observe that flood bands and fluorescent bands replicate in the two samples.

Close match between band numbers and $^{230}Th$ ages suggests the bands are likely annual. The band counted ages also match well within errors with the isochron ages.

The initial $^{230}Th/^{232}Th$ values were predicted by combining band counted ages and the errors with the uncorrected $^{230}Th$ ages. These predicted values match within error with those calculated from isochron analyses. But because of the large spread observed in the predicted initial values we cannot specifying an initial for the whole sample. We want to test this method further with more analyses.