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

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Motivation:
$^{230}$Th dating is a widely used technique for reconstructing high-resolution chronology of palaeoclimate data from speleothems (e.g. Richards & Dora, 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.

Methods:

- **Dating**
  - $^{210}$Pb and $^{230}$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).
  - $^{232}$Th 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.

**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.

**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.

**Discussion**

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.