Line Scan Methods for Quantitative Analysis of Teeth, Otolith, and Banded Iron by LA-ICP-MS

Abstract
Trace element maps give unique insight to homogeneity, enrichment, and spatial distribution of elements in solid samples. Depending on the sample type, a wealth of additional information can be gained from sample maps beyond what is available from single or multiple spot analyses or single lines/rasters. With the high spatial lateral resolution possible with the technique, LA-ICP-MS data can be used to construct trace element maps with minimal destruction of the sample. The focus of this study was to determine element and REE distribution between the banded Si and Fe mineral phases. The type of information can be used to gain insight about the underlying bedrock composition, as well as the oxygenation and elemental composition of seawater at the time the rock was formed. Human teeth were analyzed by LA-ICP-MS and cross-sectional maps were made to assess temporal variations in Pb and to monitor migration of heavy metals from dental amalgam into the teeth. Finally fish otolith elemental abundances were mapped to explore how Pb, Zn, and Cu. The molar tooth was collected from a 53 year old male.

Background
- Banded Iron Formation
  - Banded layers consist mostly of Hematite and Chert
  - Sample is from the Eastern Indian Archean Craton of Singhbhum and Orissa
  - BIF age determined by U-Pb dating of zircon grains from a volcanic ash layer immediately beneath the BIF layers.
  - The age is 3.4 billion years and makes it one of the oldest and largest BIF deposit in the World.
- Tooth Sample
  - Molar tooth containing an occlusal filling extracted in 2008 from a 53 year old male
- Fish Otolith Sample
  - The otolith sample was extracted from a 9 year old Walleye collected at Devil’s Fork on the Little Red River in Heber Springs, Arkansas. Age, weight, and length were recorded before extraction.

Sample Preparation
- All samples were mounted on a petrographic slide and thin sectioned using a Buehler IsoMet low speed saw with diamond wafering blades. Subsequent polishing of the otolith sample was performed to enable age determination and to ensure a flat surface.
- NIST SRM 2781, MACS-1 (USGS), and MAPS-1 (USGS) external calibration standards were used for calibration of the BIF, otolith, and teeth samples respectively.
- Laser Ablation and ICP-MS parameters were optimized to achieve stable signals for ubiquitous matrix elements while reducing oxides, doubly charged species and other potential interferences.

Acknowledgements
The authors would like to thank Alan Koenig (USGS), the Arkansas Biosciences Institute and the members of the Water Rock and Life lab group at Arkansas State University.

Results

![Image of elemental maps]

Figure 1. LA-ICP-MS elemental distribution maps of a 3.4 Ga BIF sample constructed from quantitative concentration data (ppm) for Fe, Si, Cr, Ni, Mg, K, Ca, Ba, Ce, and Na.

Instrument Parameters (LA-ICP-MS)

- **Laser Ablation System** - CETAC LSX-213
  - **Wavelength** 213 nm
  - **Energy** 4.5 mJ (100%)
  - **Spot Size** 200 μm (tooth & BIF), 25 μm (otolith)
  - **Pulse Frequency** 10 Hz
  - **Line Scan Rate** (BIF, Tooth, Otolith) 40, 30, 10 μm/sec
  - **Carrier Gas (Helium)** 700 ml/min
  - **Lens Voltage** 7.5 v
  - **ICP RF Power** 1500 W
  - **Nebulizer Gas Flow** 1.03 L/min
  - **Integration Time** 10 ms
  - **Detector Settings**
    - **Analog** -1625 v
    - **Pulse** 900 v

Figure 2. LA-ICP-MS elemental distribution maps of fish otolith constructed from Mg/Ca, Ba/Ca, and Sr/Ca ratios. Ratios were generated using quantitative concentration (ppm) data.

Figure 3. LA-ICP-MS elemental distribution maps of a molar tooth containing an occlusal filling generated from quantitative concentration (ppm) data. For Pb, Zn, and Cu. The molar tooth was collected from a 53 year old male.

Conclusion
- Laser Ablation is an excellent sample introduction technique for generating spatially sensitive, high resolution elemental maps for a variety of sample types.
- LA-ICP-MS elemental maps constructed using line scan methods enable point by point calibration to be possible, providing a much faster means (compared to maps compiled from single spot analyses) for obtaining sensitive and reliable quantitative concentration data.
- Using built in triggering and timing features on the LSX-213, mapping of the samples can be fully automated, minimizing user interaction times.
- Elemental maps generated for the BIF, Otolith, and Tooth samples provide a means for elucidation of elemental zoning and heterogeneity within entire sample matrices.
- Depending on the number of elements and line scan speeds and distances, data handling and processing can be time consuming.