Zinc and Copper Isotopes as Tracers of Anthropogenic Contamination in Lake Sediments

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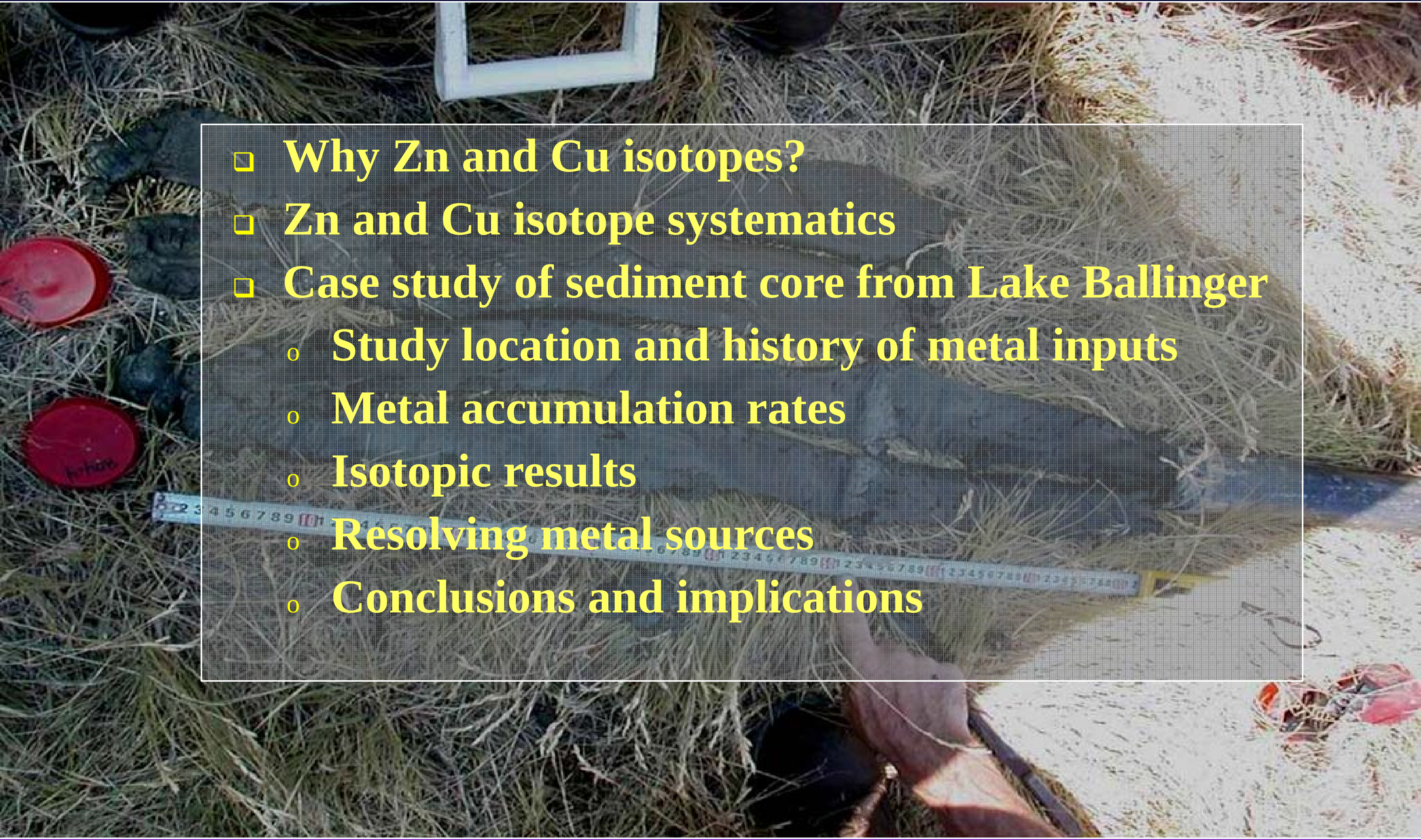
Outline

- Why Zn and Cu isotopes?
- Zn and Cu isotope systematics
- Case study of sediment core from Lake Ballinger
  - Study location and history of metal inputs
  - Metal accumulation rates
  - Isotopic results
  - Resolving metal sources
  - Conclusions and implications



Sediment core from Lake Ballinger, Seattle, WA

Why Zn and Cu isotopes?

The global atmospheric emissions of Zn and Cu are on the rise despite the fact that fluxes for other trace metals like Pb have decreased over the last 2 decades.

The sources of environmental Zn and Cu pollution are numerous (metal refining, automotive, agricultural, power generation, etc.).

- ❑ It is critical to find new environmental tracers that can fingerprint and track Zn and Cu pollution.

Zn is emitted to the atmosphere in greater quantities than any trace metal worldwide (Pacyna and Pacyna, 2001)

Zn and Cu isotope systematics

Zn Isotopes

64	48.60%
66	27.90%
67	4.10%
68	18.80%
70	0.60%

JMC 3-0749L

Cu Isotopes

63	69.20%
65	30.80%

SRM 976

- Reported in standard delta notation in parts per mil (‰)

$$\delta^{66}\text{Zn} = \left[\frac{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}}}{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{JMC}}} - 1\right] \times 1000$$

$$\delta^{65}\text{Cu} = \left[\frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{SRM}}} - 1\right] \times 1000$$

- Average $2\sigma \sim 0.07$‰

Zn isotopes

- ❑ Natural rock and water samples display only a small variation in $\delta^{66}Zn$ (Mostly between +0.1‰ to +0.4‰).

- ❑ Zn isotopes are only weakly fractionated by natural processes.

- ❑ Zn isotopes are fractionated substantially during high-temperature combustion processes (i.e., evaporation and condensation reactions).

  - Zn metal boils at 907˚C.

Cu isotopes

- Natural rock and water samples display a large variation in δ^{65}Cu, which is largely attributable to redox processes.

- Cu isotopes are fractionated <u>substantially</u> by natural processes involving oxidation and reduction.

- Cu isotopes are fractionated <u>weakly</u> during high-temperature combustion processes (i.e., evaporation and condensation reactions).

  - Cu metal boils at 2567˚C.

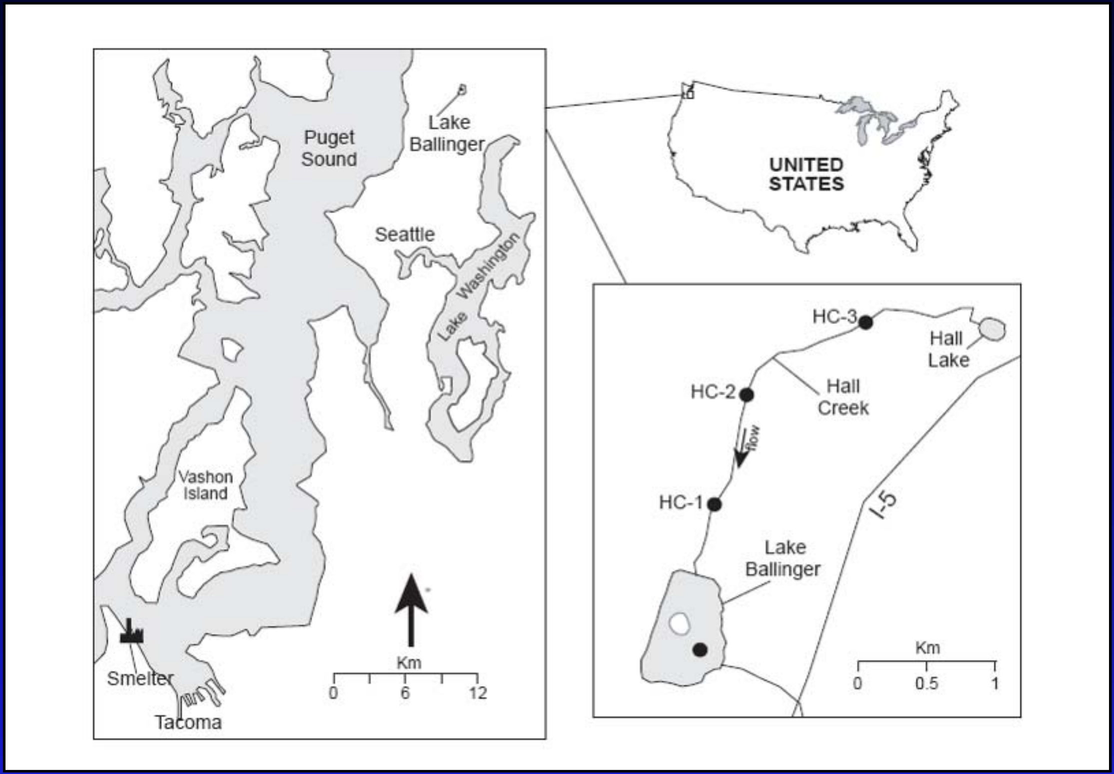
How do you measure these isotopes?

1st – It is necessary to cleanly and quantitatively separate Zn and Cu from each other and the other matrix elements.

2nd - Measure the masses simultaneously using a MC-ICP-MS instrument

Isotope analyses presented herein were conducted at the USGS labs in Denver, Colorado, and at the Department of Geological Sciences at UT El Paso.

Lake Ballinger Case Study



- Located in a highly urbanized area
- Within the range of Tacoma smelter contaminant plume

- A previous study[1] of Lake Ballinger core collected in 1998 indicated that Zn and Cu contamination was on the rise despite closure of the Tacoma smelter a decade earlier.

[1]Mahler et al. (2006) Trends in metals in urban and reference lake sediments across the United States, 1970 to 2001. Environ. Tox. Chem. 25, 1698-1709.

Lake Ballinger

Lake Ballinger Case Study

Metal contributions to the Lake Ballinger Watershed

- Tacoma smelter – Pb and Cu smelting and a major domestic supplier of As.
- Urbanization – automobile emissions, tire wear, waste burning, power generation, fertilizers, industrial inputs, storm water, etc.

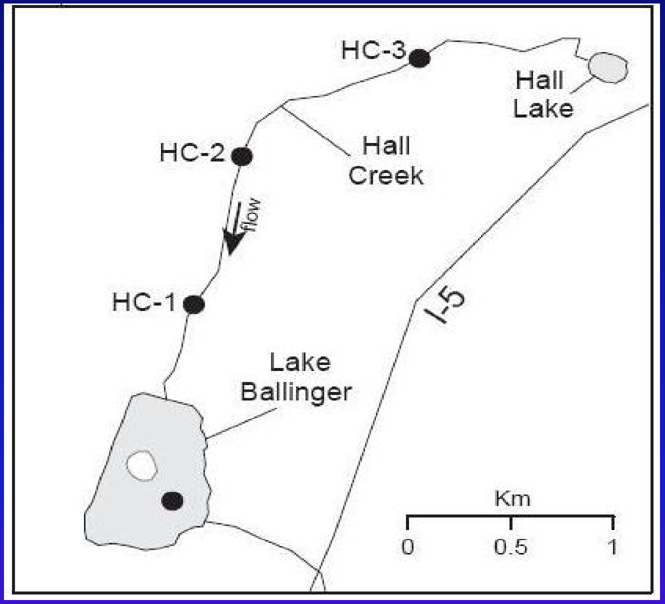
Tacoma Smelter (closed 1985). Now the Commencement Bay-Nearshore Tideflats Superfund Site

Lake Ballinger Case Study

Sampling

- In 2007 - Collected 50 cm free-fall gravity core from Lake Ballinger.
- Core was sectioned into 2 cm intervals from 0-20 cm depth and 3 cm intervals from 20-50 cm depth and prepared for multiple analyses.
- Stream-bed sediments from Hall Creek were collected from three locations.
- Ages were estimated using the ^{210}Pb profile and applying the constant rate of supply model (^{137}Cs was used as a check).

Sample locations



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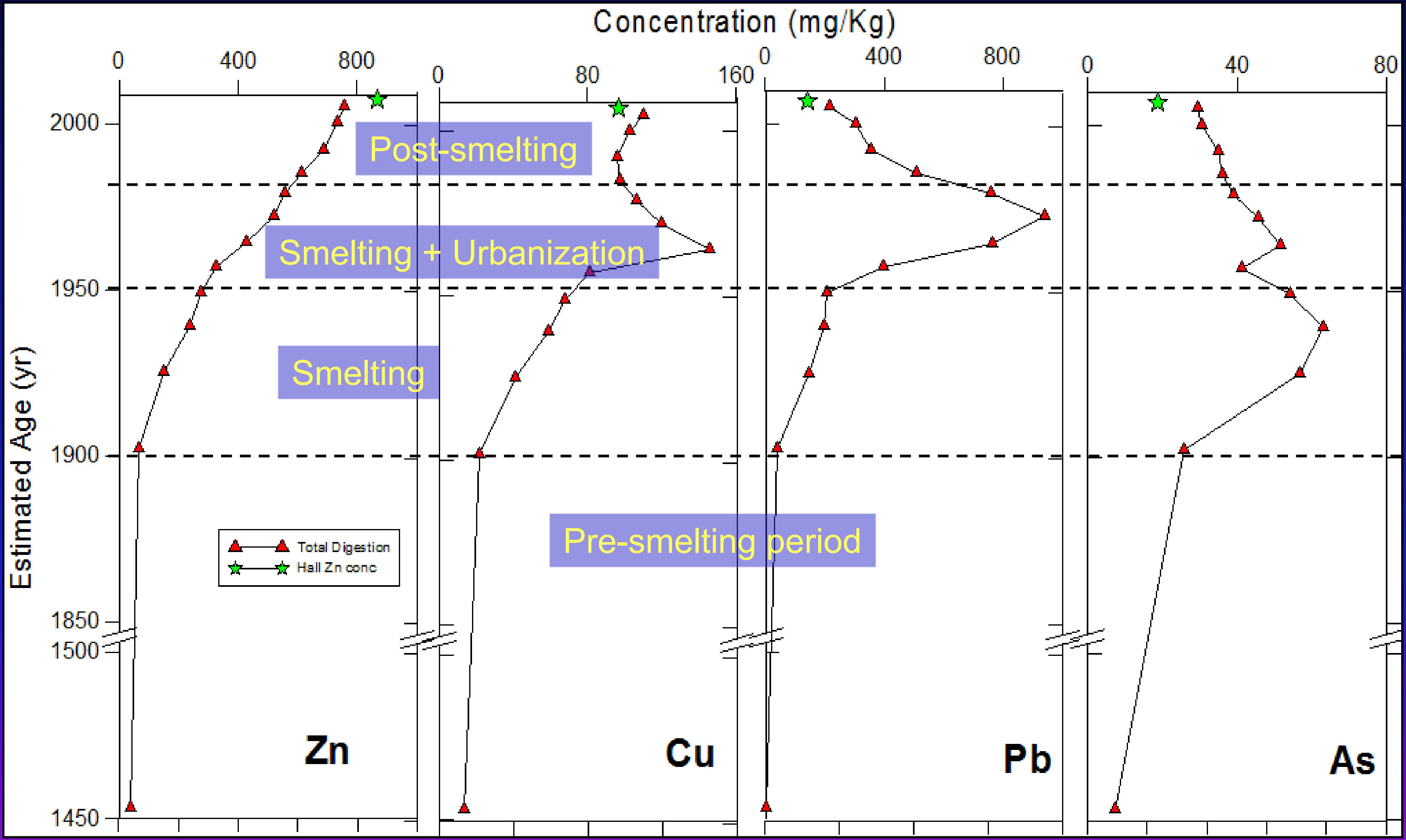
Concentration profiles for Zn, Cu, Pb, and As



*** Concentration data alone cannot distinguish metal sources**

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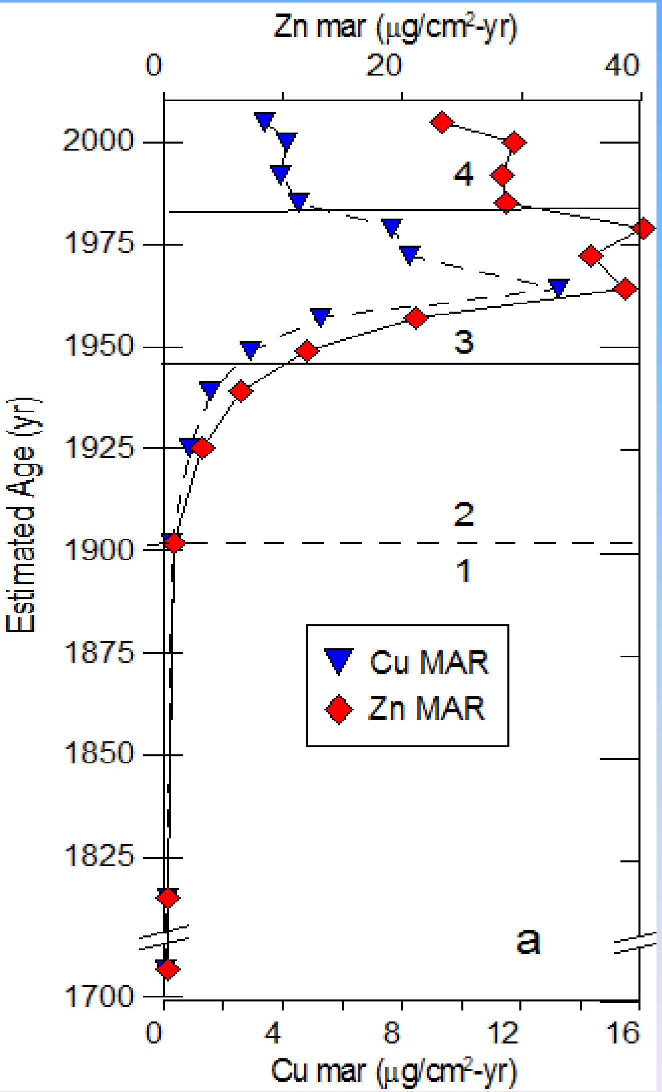
Zn and Cu Mass Flux

Sediment core

0 cm

25 cm

50 cm



Post-smelting

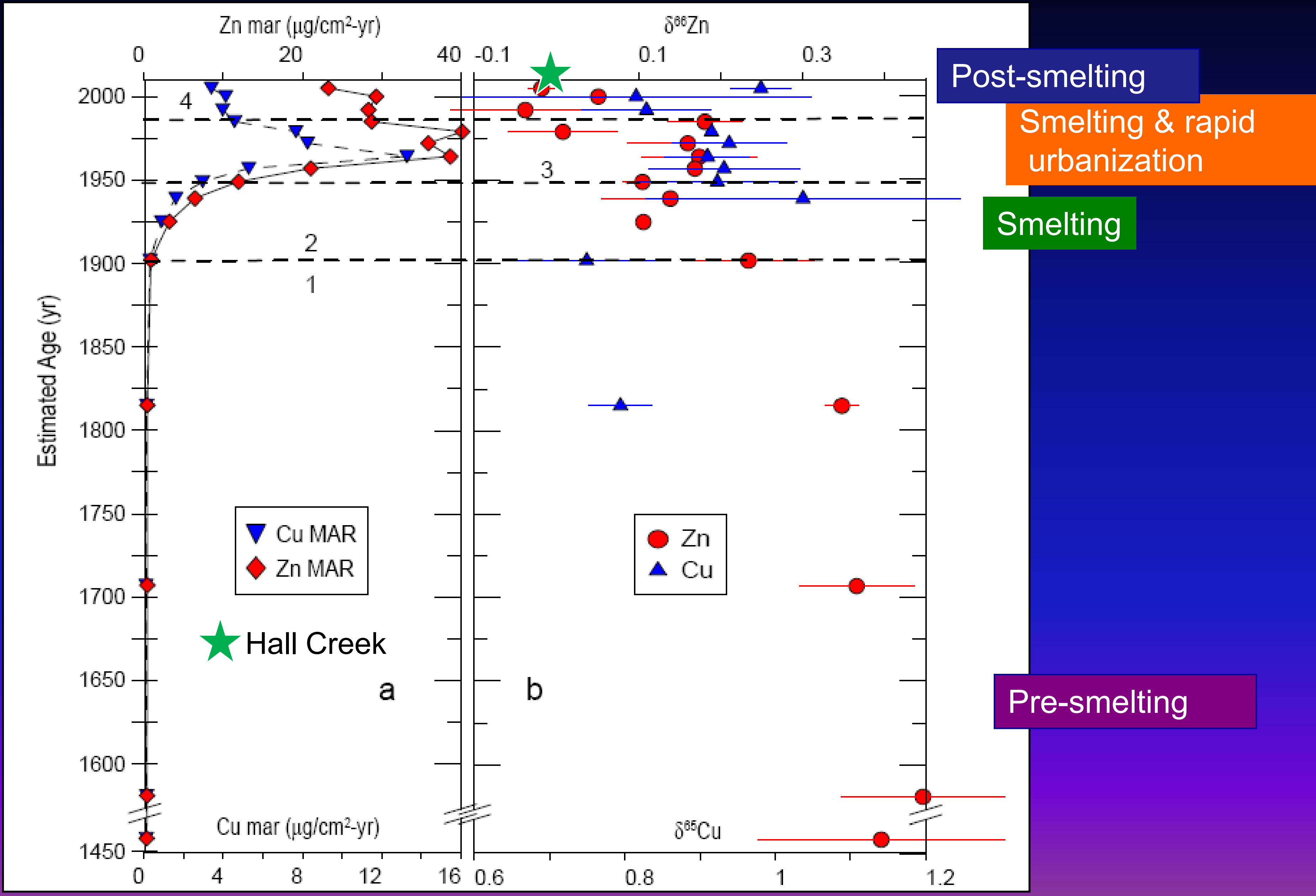
Smelting & rapid urbanization

Smelting

Pre-smelting

Mass Accumulation Rates (MARs) are calculated by multiplying the sedimentation rate by the metal concentration

δ66Zn and δ65Cu of sediment samples



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Key Zn and Cu isotope results

- The $\delta^{66}Zn$ and $\delta^{65}Cu$ for the pre-smelting period (i.e., natural metal inputs) are easily distinguished from anthropogenic metal sources.
- The $\delta^{66}Zn$ and $\delta^{65}Cu$ of sediments during the rapid urbanization period are similar to those from the smelting period, suggesting that the added metal input came from remobilization of historically contaminant soils.
- The “light” $\delta^{66}Zn$ found in the post-smelting sediments and in Hall Creek (0.02 ± 0.06‰ 2σ) is likely from urban runoff.
- The $\delta^{65}Cu$ for the most recent post-smelting sediments is “heavy”. SSD work suggests that this is related to changes in Cu-organic complexation during diagenesis

Lake Ballinger Case Study

Sources for Zn (and Cu) contamination

- Possible sources are numerous and include galvanized steel, automobile emissions, tire wear, oil leakage, power plants, and fertilizers.
- We suspected tire wear was an important contributor because tire rubber contains about 1 wt% Zn and Lake Ballinger is situated between two major highways.
- Zn isotopes for five different tires ranged from -0.1‰ to +0.14 ‰ and averaged +0.04 ‰ ± 0.2 ‰.

The δ^{66}Zn of tires overlaps with the δ^{66}Zn of the urban Zn source.

For more information, see:

Thapalia, A., Borrok, D.M., Van Metre, P., Musgrove, M. (2010) ***Zn and Cu isotopes as tracers of anthropogenic contamination in a sediment core from an urban lake***. ES&T 44, 1544-1550.

Implications

- Zn (and probably to a lesser extent Cu) isotopes can be useful for evaluating contaminant trends in sediment core.
- These metal isotopes can resolve anthropogenic and natural metal sources.
- In some cases they can be used to distinguish among the different sources of urban pollution.

CURRENT PROJECTS

- Using Zn isotopes to identify fertilizer contributions in river systems.
- Assessment of Zn isotopic fractionation during coal and coal+tire combustion.
- Using Zn isotopes to elucidate metal attenuation mechanisms in soils.

Elephant Butte Reservoir, NM

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