

# Major and Minor Element Variations in Speleothems as a High Resolution Paleoclimatic Record

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Cave calcite deposits or speleothems collected from California Caverns in Calaveras County, California show strong potential for preserving a high resolution paleoclimate record. Geochemical variations along speleothem growth axes combined with precise U-series dating will provide a continuous high temporal resolution record of precipitation and temperature changes in California as far back as the last glacial maximum (LGM), about 18,000 years ago. Major and minor element x-ray fluorescence analysis performed on beamline 10.3.2 at the Advanced Light Source will be combined with O ( $^{18}\text{O}/^{16}\text{O}$ ), C ( $^{13}\text{C}/^{12}\text{C}$ ), and Sr ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) isotopic analyses of microdrilled samples. The high spatial resolution and elemental sensitivity of this beamline provide an ideal tool for the detection of temporal variations in speleothem composition. As a typical speleothem growth rate is about 50  $\mu\text{m}/\text{year}$ , the x-ray beam allows at least an annual time resolution. The age of the samples will be precisely determined using  $^{230}\text{Th}/^{234}\text{U}$  TIMS analysis. Previous studies have shown that oxygen isotope ratios can be used to determine past temperature changes (Dorale et al., 1992). Carbon and strontium isotopic variations will be interpreted as indicating changes in groundwater flow path related to changes in recharge rate. A continuous record of major and minor element variations will provide a valuable supplement to this isotopic data.

The main sources of speleothem Sr and C, soils and bedrock, commonly have distinct isotopic signatures. Soil carbon isotopic variations may be caused by shifts between  $\text{C}_3$  and  $\text{C}_4$  vegetation. However, we have chosen a site in which vegetation has been constant over the time scale of interest. Therefore, C and Sr isotopic variations likely reflect changes in solute transport and water-rock interaction due to hydrologic changes. Initial results suggest that the two main sources of speleothem C and Sr, overlying soils and bedrock, have distinct isotopic signatures. Therefore, through the measurement of  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{13}\text{C}$  for all soil, bedrock, and cave calcite samples, we can, check for any vegetation induced changes as the two systems would be expected to co-vary under constant  $\text{C}_3$  influence. The C and Sr isotopic systems will thus be useful for determining changes in water-rock interaction. Past changes in flow regime should be reflected by the degree to which water in equilibrium with the soil equilibrated with the bedrock before the signal was preserved in a speleothem. Banner et al. (1996) determined that in a cave system in Barbados, during times of high precipitation, groundwater flow through the bedrock was mainly conduit flow and hence the water retained more of a soil signature, whereas during times of low precipitation, diffuse flow dominated and the water contained more of a bedrock component. In order to interpret C and Sr isotopic variations along speleothem growth axes, we will apply the model of Johnson and DePaolo (1994) which relates the temporal isotopic evolution of groundwaters to solute transport and water-rock interaction. It is likely that both major and minor element variations between speleothem growth bands also reflect the hydrologic conditions at the time of formation. If the concentration of these elements varies between the soil and bedrock, we should see more of a soil component during times of high precipitation and more of a bedrock component during times of low precipitation. Through the

use of the soft x-ray beamline 10.3.2 at the ALS, we have initially examined the temporal variation of Ca, Mg, Sr, and Fe within a stalactite. Figure 1 shows the variations in iron concentration along a speleothem growth axis. The bands of high iron concentration most likely correspond to detrital layers deposited by flood waters. The bands are visible in the sample as well, but the elemental analysis helps us distinguish these bands from similar reddish bands caused by the presence of organic acids. Figure 2 shows that the iron bands are indistinguishable from the  $\text{Fe}_2\text{O}_3$  standard. Thus, these iron bands were deposited in an oxidizing environment.

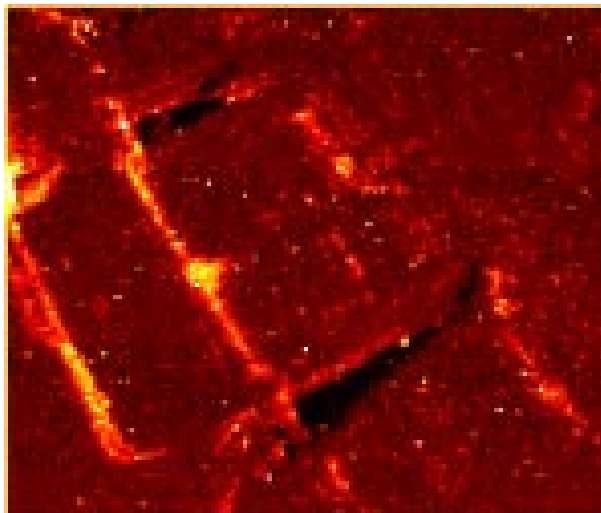


Figure 1. X-Ray Fluorescence map of Fe in a stalactite. Bands of high Fe concentrations are shown by the light areas.

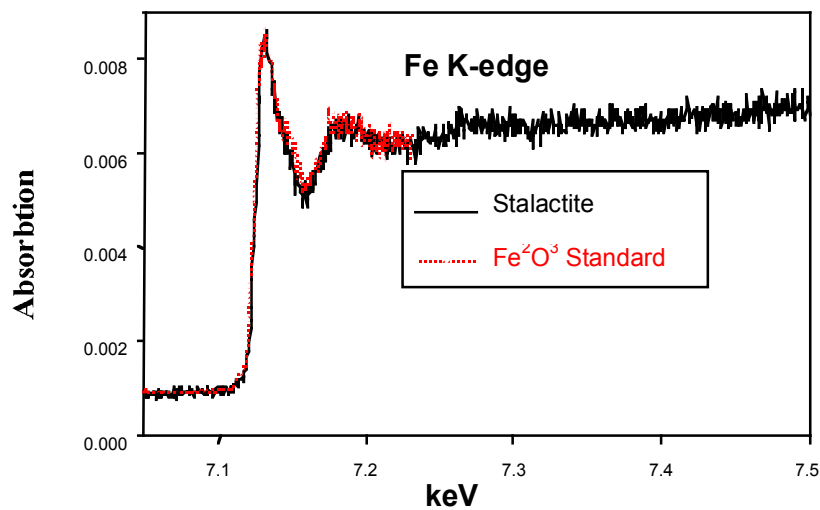


Figure 2. The absorption spectra of Fe in the stalactite is compared to an  $\text{Fe}_2\text{O}_3$  standard.

The initial results are promising, but more samples need to be analyzed. In addition, we need to measure these elements in stream water in the drainage basin, in the soil, in cave drip waters, and in the limestone bedrock in order to fully understand the complex interactions governing the concentration of these elements in the calcite. High resolution time series such as these are very important in understanding the natural variability of the climatic, hydrologic, and ecologic systems in California on long time scales. This information may help lead to improved climate models and hence improved predictions about future climate changes. Speleothems potentially contain the most complete record of past environmental change in central California, and their study will provide a valuable complement to other climate records.

## REFERENCES

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