CO_2 Clumped Isotopologue Thermometry to Study Natural and Synthetic Carbonates

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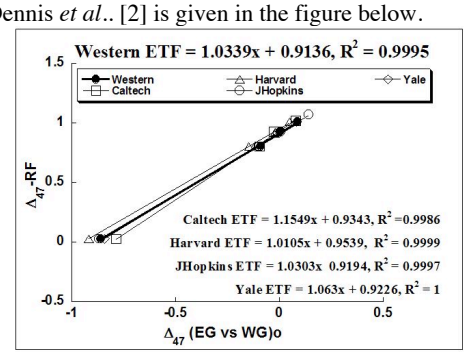
The distribution of rare "clumped" isotopologue species in the carbonate lattice is temperature dependent [1]. Our primary interests lie in exploiting this feature of clumped isotopologue science to explore paleoenvironments. We have established protocols to calibrate the clumped isotope thermometry of CO_2 by defining an absolute reference frame based on CO_2-H_2O equilibration experiments conducted at 10ºC, 25ºC, 50ºC and 1000ºC. A plot of experimental and theoretical equilibration intercepts has yielded an empirical transfer function (ETF) for our lab. A comparison of our ETF with Dennis *et al*.. [2] is given in the figure below.



Application: Seeds from the hackberry tree (*Celtis occidentalis*) precipitate up to 70 wt. % aragonite in their endocarp. Fossil hackberry seeds have been recoved from Holocene deposits across most of N. America and have great potential as a terrestrial paleoclimate proxy. The determination of growth temperature by clumped isotopologue analysis of the seed carbonate is the first application of this emerging field to hackberries. Seed samples were obtained from 4 different locations in N. America with differing climatic conditions. Growth temperatures were calibrated using a regression developed for synthetic carbonates grown from 4 to 45ºC and analysed for clumped isotopologues. This study demonstrates the potential of the isotopologue technique to terrestrial paleotemperature estimates, which can be used to estimate the $\delta^{18}O$ values of plant waters and ancient relative humidity conditions.

[1] Ghosh *et al*. (2006) *GCA* **70**, 1439-1456. [2] Dennis *et al*. (2011) *GCA* **75**, 7117-7131.

Authigenic and exogenic mineral particles in lung tissues.

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Investigation of mineral particles by SEM and TEM in samples of lung tissues from 34 subjects who lived in the urban and industrial region of Upper Silesia, Poland, revealed the occurrence of 15 mineral species. Based on their origin inferred from chemical compositions, structural properties, and morphological features, mineral particles can be grouped into authigenic and exogenic, i.e. inhaled dust particles.

Authigenic biocalcite and Mg-biocalcite (mean-diameter <1.5 μm) are age-related ranging from 5.5 to 64.62 vol.% of mineral matter in dry lungs. They often envelop exogenic particles masking their presence. The biocarbonates formed preferably in lungs of non-smokers. The largest of all mineral particles (mean diameter > 2,5 μm) are bioapatites observed exclusively in lungs of male cigarette smokers and formed in response to pathogenic processes in lungs. Ferrihydrate and goethite are products of redox-driven reactions in lungs.

Mineral composition of exogenic particles reflects the mineral compostion of atmospheric dust particles in the Upper Silesia. The inventory of abundant anthropogenic mineral particles includes: amorphous aluminosilicates, mullite, Fe-oxides, barite, trydymite, REE-phosphates metallic Fe, metal alloys, and (Zn, Fe, Pb)-sulfides. Minerals derived from natural sources and indicative of long-range transport include: micas, feldspars, pyroxenes, and amphiboles. Quartz particles are both natural and anthropogenic.

While the amount of authigenic carbonates increases with age the opposite trend is observed for aluminosilicates, silica, Fe-oxides, and metal alloys in individuals age 70 and older. The amount of barite in lungs of those individuals doubles relative to younger individuals.

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