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SR-micro XRF and Transmission Electron Microscopy: advances in the accuracy of past climate and environmental interpretation from carbonate crystals data.

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Investigation by high resolution Synchrotron-Radiation based micro X-ray fluorescence (SR-μXRF) at the Australian Synchrotron coupled with Transmission Electron Microscopy (HR-TEM) and both terrestrial and marine carbonates imposes uncertainties on the boundary between stages of crystal nucleation and growth and diagenetic processes. This has profound implications on the correct (accurate) interpretation of chemical data that are proxies of climate parameters are interpreted. An accurate interpretation of climate proxies is necessary when such proxies are transformed into temperature or rainfall quantitative data that are used to validate climate models.
In the last 20 years, speleothems (defined as cave secondary mineral deposits) consisting of calcium carbonate have proven to be exceptional archives of past climate and environmental changes that parallel ice cores for their accuracy. However, amongst many published speleothem-based records, there are uncertainties that lead to anecdotal evidence. This may generate skepticism in the quality of data, particularly by modelers who do not have knowledge about how proxy data are captured by speleothem (or ice) crystals. Such knowledge is grounded on a thorough nanoscale investigation of crystallization processes.
HR-TEM investigation of in-situ products of in-situ crystallization experiments suggest that there are many pathways leading to speleothem carbonates formation, which capture chemical species differently. This translates into concentrations of elements that defy thermodynamic partitioning. When chemical concentration variabilities of trace elements are interpreted without knowledge about how these are incorporated in the final product of crystallization, interpretations are uncertainty-ridden.
Most carbonates used to reconstruct past climates and environments grow via particle-mediated and/or formation of metastable phases. By contrast, the classical ion attachment to growth sites theory appears to be defied by free-energy barriers. The occurrence of diverse pathways and, consequently, the climatic significance of climate proxy data incorporated in speleothem crystals is detected through nano- and micro-scale techniques.
Through HR-TEM observations of "instant" cave precipitates, we found that organic compounds and particulate influence the way hydrological markers, such as Sr, are incorporated in different crystal fabrics. SR-micro XRF mapping of stalagmites from the Indo-Pacific region show that Sr is an annual hydrologic marker and, commonly, an increase in its concentration occurs in compact (non-porous) calcite. This phenomenon is indicative of dry conditions. However, we also documented Sr concentration increase in layers consisting of porous fabric. This fabric is commonly formed during wet conditions. The discrepancy, which was highlighted by using SR-micro XRF mapping, was solved by documenting crystal growth from fast and slow drips at the nanoscale in the cave where speleothem show Sr increase in porous fabrics. Fast drips (representative of "wet" conditions) yielded calcite nanocrystals bridged by amorphous particulate rich is Si, K, and Al. This likely originated from silicate weathering and, thus, includes the excess Sr within the open fabric. The presence of particulate itself also inhibits coalescence of nanocrystals, leaving porosity in between the growth units.
We will show examples of how SR-micro XRF mapping enhances the power of petrography and geochemistry as palaeo-climate tools and how High-Resolution Transmission Electron Microscopy is a necessary complementary technique. Our examples will briefly touch the origin of other carbonates whose formation through nanoscale attachment has revolutionized Earth's history.

Speakers Gender

Female

Travel Funding

No

Level of Expertise

Expert

Do yo wish to take part in the poster slam

No

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