Mn coordination and distribution in foraminiferal calcite under varying environmental conditions

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Benthic foraminiferal Mn/Ca, though often referred to as an indicator of authigenic contamination, has recently been suggested as an indicator of bottom water oxygen levels. However, our understanding of how Mn is incorporated into benthic foraminifera is incomplete, and roles of potential contaminant phases need to be clarified. To evaluate whether Mn can indeed be used as a proxy for past hypoxia, it is important to understand where and how Mn occurs in benthic foraminifera, such as whether it is incorporated into the calcite as a Mn-bearing carbonate, and whether other forms of Mn are present. It is also important to evaluate how/whether changing environmental conditions and vital processes may affect Mn coordination and distribution.

We use synchrotron methods (X-ray absorption spectroscopy (XAS) and µ-X-ray fluorescence (µXRF) mapping) to evaluate how Mn is incorporated into the calcite lattice (its distribution and coordination) in benthic foraminifera. We complement this with solution ICP-MS to determine mean Mn/Ca values for pooled foraminifera from the same samples. We use field-collected samples of living benthic foraminifera (to avoid diagenetic effects) from two known oxygen conditions, allowing us to evaluate whether differing environmental conditions affect Mn distribution and coordination.

Spectral data (XAS) indicate that Mn in the foraminiferal tests occurs as a Mn-carbonate, while small points of external debris with high [Mn] in these uncleaned foraminifera generally have Mn-oxide-type spectra (suggesting these can be removed via cleaning methods). µXRF maps show that in many species, [Mn] is fairly evenly distributed at low or moderate concentration throughout the test, potentially suggesting stable oxygenation conditions. However, other species have specific chambers (representing a certain time) with elevated [Mn], perhaps suggesting intervals of greater oxygen stress or a response to vital processes that alter the microenvironment.