European Mineralogical Conference
Vol. 1, EMC2012-260-1, 2012
European Mineralogical Conference 2012

Sr, Cu and Zn incorporation in earthworm synthesized calcium carbonate granules - a μ-XAS and μS- XRF investigation

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Earthworms (Lumbricus terrestris) have been cultivated in metal contaminated soils collected from former mining sites (Yates, Cymnwyth and Devon Great Consols, UK) and metal amended soils. The earthworms produce granules which are biomineralization products comprising the calcium carbonate polymorphs vaterite, aragonite, calcite and amorphous calcium carbonate. This study looked at the trace metal chemistry within the granules using micro X-ray absorption spectroscopy (μXAS) and synchrotron X-ray micro-fluorescence (μS-XRF). Structural speciation studies have been performed on Sr, Zn and Cu using XAS with XRF providing spatial distribution and Mn, Fe, Pb and As were also mapped with XRF.

Concentric zoning is observed within the granules for Sr and Mn. Analysis of Sr K-edge XAS data from the granules indicates that Sr replaces Ca in the crystal structures of the carbonate polymorphs. In contrast to Sr, Zn is located around the granule margins and Zn XANES spectra indicate that Zn can be incorporated as adsorbed species on calcite, structurally bound within the calcite lattice or as discrete hydroxycarbonate phases such as hydrozincite. Cu appears to be heterogeneously distributed (as is Fe, Pb and As) with no chemical association to the calcium carbonate, but is present as inclusions mainly in its original soil-based form.

Of the three metals studied Sr has much the highest affinity for biomineralized carbonates and is incorporated to higher concentrations (3.4 wt %) than has previously been reported for either inorganic and biogenic calcites. This suggests that earthworm granules may play an important role in Sr immobilization and its biogeochemical cycle, but have a much lesser role for Zn and Cu. The incorporation of the contaminant metals in the carbonate granules is a function of their bio-availability (i.e. their chemical speciation in the soil, and porewater), their chemistry within earthworm calciferous glands and also of the reaction mechanism (bio- and/or inorganic) by which these carbonates are formed.