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Micro-Raman spectroscopy of nanomaterials: applications in archaeology

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Micro-Raman spectroscopy of nanomaterials: applications in archaeology.

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SUMMARY

"Nanomaterials" is a generic term used to describe nano-sized crystals and bulk homogenous materials with a structural disorder at the nanoscale. Ancient (and modern) ceramics and glasses derive some of their properties (eg. pliability and low sintering temperature) from the fact that their raw material namely natural clay is nanosized. Furthermore the pigments used to colour ceramics and glasses need to have particle sizes <500 nm for the object to appear homogenously coloured to the human eye. Raman spectroscopy intrinsically probes chemical bonds and is therefore one of the few techniques that has been proven useful to provide information at the nanoscale. It is an excellent tool to study ceramics and glasses as a Raman spectrum can be used to identify phases, analyse amorphous domains in the silicate network and identify pigments on a nano-scale. The characteristics of a glass, ceramic or ceramic glaze derived through its Raman spectrum can then be linked to the technology used to produce an artefact and in this way provide information about its relative age and provenance. Likewise, the identification of pigments and binders in San rock art might provide information about production techniques and assist in the developement of conservation procedures.

In this thesis micro-Raman spectroscopy (with X-ray fluorescence, X-ray powder diffraction, electronmicroscopy and photoluminescence as supportive techniques) was utilised to study archaeological artefacts from the Mapungubwe Collection and San rock art. It was possible to re-date celadon shards excavated on Mapungubwe hill in 1934 to the Yuan or even later Ming dynasty in stead of its original classification as Song. A profile of the glass technology used to produce the Mapungubwe oblates, small trade beads from the "royal burials" on Mapungubwe hill was determined and quite a few unique characteristics of the beads may eventually help to establish their provenance. The possible influence of the presence of *rock hyraces* at rock art sites on the deterioration of rock art were investigated and during the study very rare polymorphs of $CaCO_3$ (vaterite and monohydrocalcite) were discovered in rock hyrax urine. This study was extended to analyse a San rock art fragment and another first was the identification of animal fat on the fragment, but the exact origin of the fat has to be verified by similar experiments.

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