This study was initiated on a field trip to the Mapungubwe Heritage site in December 2001 under the leadership of Prof. Andri Meyer (Archeology Department, University of Pretoria), who spent a large part of his life excavating the Mapungubwe archaeological site. The other team members were Prof. Ian Meiklejohn (Department of Geography, Geoinformatics and Meteorology of the University of Pretoria) and Isabelle Barrier (see photo's in article), at that time an Archaeology student from the University of Pretoria.

**The results of this study were presented as a poster contribution at the *3rd International Conference on the Application of Raman Spectroscopy in Art and Archaeology* held in Paris, 31 Aug. –3 Sept. 2005 and the full results published in the Journal of Raman spectroscopy and follows as chapter 5.**

**L C Prinsloo, Rock hyraces: a cause for San rock art deterioration?**

**The poster won a Young Investigater's award at the conference**

The unique properties of hyrax urine and its use as traditional medicine that came under my attention during this study motivated me to send a hyraceum sample to Prof. Anna Jäger, Department of Medicinal Chemistry, University of Copenhagen, Denmark. She tested the sample for affinity to the GABA-benzodiazepine receptor and obtained a positive result, which supports its use as traditional medicine for the treatment of epilepsy. In order to establish if there is a connection between the hyrax diet and the activity of the samples we asked Prof. Louis Scott if we could use samples from his large collection of hyraceum samples, collected in different biomes, for further testing. The results from this study are published in an article and were presented at an international conference.

**Jäger AK, Olsen A, Prinsloo LC and Scott L. 54th Annual Congress on Medicinal Plant Research, 29 August-2 September, Helsinki, Finland. Planta Medica, 2006, 72: 993.**

Andreas Olsen, Linda C. Prinsloo, Louis Scott and Anna K. Jäger, Hyraceum, The fossilised metabolic products of rock hyraces, shows affinity to the GABA-benzodiazepine receptor, *South African Journal of Science* 2007; **103:** 437.

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# Rock hyraces: a cause of San rock art deterioration?

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**San rock art sites are found throughout southern Africa, many showing signs of deterioration. In order to conserve this invaluable heritage, a long-term multidisciplinary project has been launched to monitor the rate of their deterioration and determine the various chemical processes that are possibly contributing to the decay. This study was initiated to establish if Raman spectroscopy could contribute to this project and since rock hyrax colonies live in close proximity to many of these archaeological sites, the possible influence of their metabolic products on the deterioration process was investigated.**

**The precipitates from the urine of rock hyraces were analysed with Raman and Fourier-transform infrared (FTIR) spectroscopy. Where the urine was in contact with the faeces, the precipitates are a mixture of vaterite (a rare polymorph of $CaCO_3$) and the hydrated salt calcium monohydrocalcite (also rarely found in nature). On areas where this contact is at a minimum the common and stable polymorph of $CaCO_3$, calcite, is the main component. SEM micrographs and XRD analysis support the Raman and FTIR results.**

**XRD, FTIR and preliminary GC-MS analyses of hyraceum, the fossilised mixture of faeces and urine, identified an inorganic phase (potassium chloride, with small concentrations of other salts, e.g. vaterite and weddelite) and an organic phase, which is a cocktail of various aromatic compounds, mainly amides, alcohols and acids. These compounds could contribute to the crystallisation of these rare carbonates, as well as other uncommon salts detected on the cave walls, such as syngenite. The presence of phosphates in the urine may further act as a stabilizing agent. Copyright © 2007 John Wiley & Sons, Ltd.**

**KEYWORDS:** vaterite; monohydrocalcite; syngenite; oxalate; rock art

## INTRODUCTION

The hyrax is so unlike other animals that although evolutionarily linked to elephants and sea cows, it is placed by itself in a separate order, namely Hyracoidea.[1] They are primitive subungulates that have changed in the course of evolution from ancestral fossil forms that have been found in the early Oligocene deposits (35 millions years ago) of the Egyptian Fayum region.[1] Rock hyrax (*Procavia capensis*) is one species of the genus *Procavia* and is distributed all over Africa. They are of considerable economic importance to the African people as food, as well as for their pelts.[1]

The small stockily built mammals are about the size of a rabbit with short legs, a rudimentary tail and small rounded ears (Fig. 1(a)). They are gregarious animals and huddle together at night under rock overhangs or in caves, while most of their day is spent basking in the sun, continuously on the lookout for avian predators.[2] The soles of their feet are naked, having a thick skin padded with glandular tissue that exudes and keeps the surface permanently moist.[1] This enhances the traction of their feet and enables them to move with great agility across rock faces, covering it in time with a hard black layer.

They are mixed feeders, selecting phenological stages of all their food plants to obtain the required diet and utilising plant parts most advantageous to them during a particular season. They eat a variety of grasses, forbs and shrubs, including some that are highly aromatic and others known to be poisonous to other species.[1]

Hyrax intestinal tracks have certain features that are unusual among mammals. Posterior to the stomach, and connected to it by the small intestine, they have a large sac in which cellulose in food is broken down by fermentation. Posterior to and connected to the sac by a short length of intestine is a fermentation chamber (caecum), which produces short-chain fatty acids (acetic acid: 63.9%, propionic acid: 22.9% and butyric acid: 6%) at a rate of nearly 10 mmol/100 ml/h to serve as an energy source.[3]

They urinate and defecate in latrines, which occasionally through continued use may assume very large proportions.[1]

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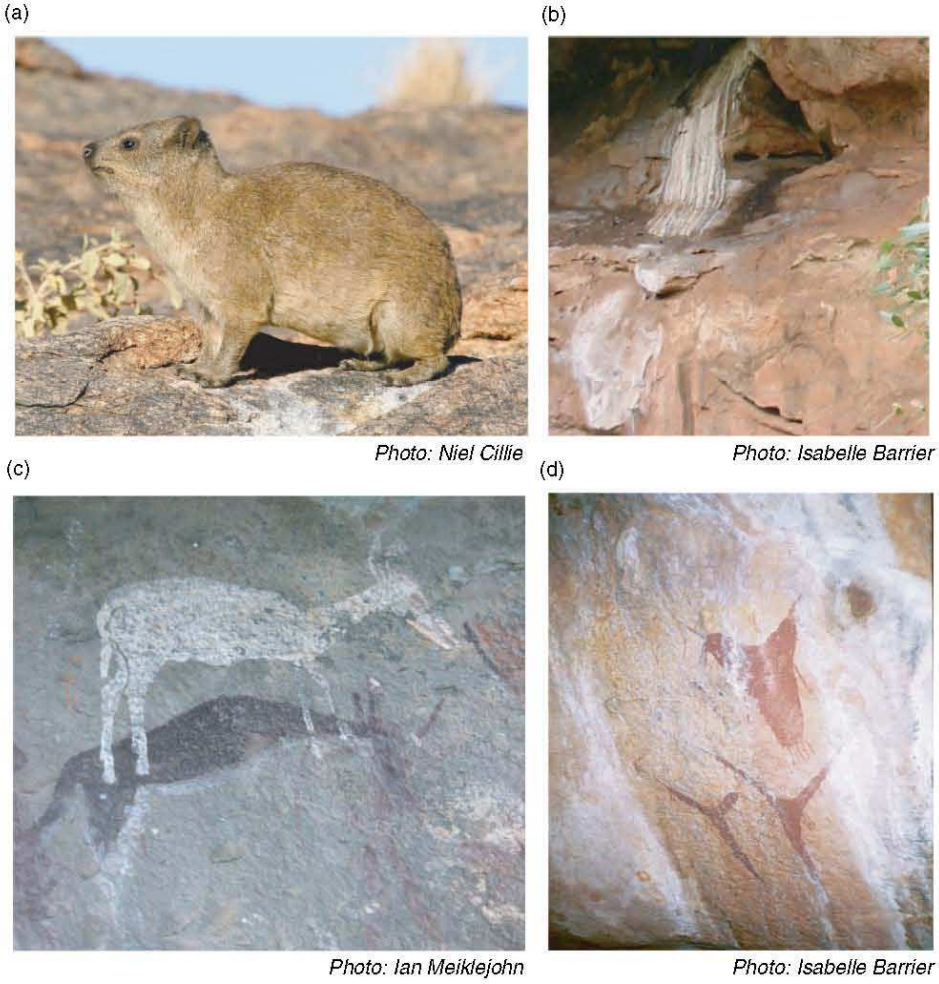


**Figure 1.** (a) Rock hyraces (*Procavia capensis*); (b) Rock hyrax urine in cave inhabited by rock hyraxes; (c) Rock painting (Battle cave, Injisuthi valley, Kwazulu Natal Drakensberg) of a buck transcending to the spirit world upon slaying; (d) White precipitates defacing San rock art in Venus shelter (Mapungubwe National Park), believed to have been used for initiation rites.

The urine crystallises as a white precipitate (Fig. 1(b)), and where the urine and faecal pellets mix, a thick black resinous crust is formed, which in the dry arid regions of South Africa can accumulate and become metres thick. This substance is called 'dassiepis' (Afrikaans vernacular) or hyraceum and is still being sold as traditional medicine in South Africa and exported to France for use as fixative in the perfume industry. Embedded in the fossilised hyraceum are animal hairs and plant remains, which form an invaluable DNA record and palæo-environmental history that stretches back millions of years and has been used in various studies to determine the variation in the plant population due to climatic changes.[4–6]

Rock hyraces and their genetic predecessors were part of the African landscape for millions of years, and when the earliest hominid species made their first appearance, they vied with the rock hyraces for the same caves and overhangs as shelters. The, in many instances, Clarens Formation sandstone cave walls provided a canvas for their San (previously known as Bushmen) hunter-gatherer descendents, whose paintings reflect their history and spirituality over a 25 000 year time span (Fig. 1(c) and (d)).

San rock art sites are found throughout southern Africa; unfortunately this heritage is rapidly being lost through natural weathering processes, which is a cause of concern to many researchers.[7] In order to develop techniques for its preservation, a long-term multidisciplinary project has been launched to monitor the rate of their deterioration and determine the various geological, chemical, mechanical and biological processes that are possibly contributing to the decay. Since rock hyrax colonies live and have lived in close proximity to many of these archaeological sites, the possible influence of their metabolic products on the deterioration process will be taken into account.

Raman spectroscopy has been used successfully to analyse pigments and substrata in prehistoric rock art,[8–12] and in this study its usefulness as a complementary technique in the study of San rock art deterioration is explored for the




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first time. Specifically, rock hyrax urine and faeces were analysed with Raman and Fourier-transform infrared (FTIR) spectroscopies and XRD measurements. A few crystalline samples collected on the cave walls at rock art sites in the Mapungubwe National Park were also studied.

## EXPERIMENTAL

### Samples

A sample of the precipitates of rock hyrax urine was collected outside a cave in the Mapungubwe National Park situated at the confluence of the Limpopo and Shashe rivers, South Africa. It formed part of a multidisciplinary study to determine the condition of the San rock art in the area and to determine whether Raman spectroscopy could play a role in future studies in this regard. Samples of crystalline growths were collected on rock faces that showed signs of weathering, and as at all the rock art sites a strong pervading smell indicated the presence of rock hyraces, their urine precipitates (Fig. 1(b)), in appearance very similar to the crystal growths deforming the rock art (Fig. 1(d)), were also collected.

Urine samples, used for verification purposes, were collected in the Karoo and Gamkaskloof National Parks, Western Cape Province. Fresh samples were obtained from the National Zoological Garden, Tshwane, South Africa. The hyraceum sample was collected near Richmond in the Karoo.

### Experimental techniques

Raman spectra were recorded on an XY Raman spectrometer from Dilor using the 514.5 nm line of a Coherent Innova 90 $Ar^+$-laser as exciting radiation. The sample was pressed into a KBr pellet to reduce fluorescence and the spectra were recorded in a back-scattering configuration with an Olympus microscope attached to the instrument. The spectral resolution for all the measurements was 2 $cm^{-1}$. Optimum recording conditions were obtained by varying the laser power, microscope objective and size of the confocal hole.

A Perkin-Elmer FTIR spectrometer was used to record the mid-infrared transmission spectra. The resolution was 2 $cm^{-1}$ and 32 scans were signal-averaged in each interferogram.

Powder X-ray diffraction data was recorded with a Siemens D501 automated diffractometer equipped with a secondary graphite monochromator. The applied potential was 40 kV and the corresponding current 40 mA. Cu K$\alpha$ radiation was used as the primary X-ray beam. A pattern was recorded from 3 to 70° (2$\theta$) in steps of 0.05°. The measuring time was 1 s and the scanning speed 3°(2$\theta$) per minute.

Electron micrographs were obtained using a JSM-6000F scanning electron microscope (JEOL, Tokyo, Japan).

Luminescence spectra of rock hyrax urine were recorded at room temperature (monochromator: HR 640, Jobin Yvon; photomultiplier: TE-10-RF, Products for Research Inc.) using He–Cd (325 and 442 nm), $Ar^+$ (514.5 and 488 nm) and He–Ne (632.8 nm) lasers as excitation sources.

## RESULTS

### Rock hyrax urine

Initial attempts to obtain the Raman spectra of the crystalline precipitates from the urine were unsuccessful owing to a large fluorescence background excited by the 514.5 nm laser line. Since dilution of a sample in an inert matrix helps to reduce fluorescence, the urine sample was pressed into a KBr pellet. In the visual mode of the microscope attached to the Raman instrument, small round spheres imbedded in the KBr matrix could clearly be distinguished. A combination of the 100× objective of the Olympus microscope attached to the Raman instrument and a small confocal hole made it possible to record the spectra on individual spheres. Two unmistakably different Raman spectra were obtained indicating that the spheres were chemically distinct (Fig. 2(a) and (b)).

The spectra identified the two crystalline phases as vaterite and monohydrocalcite. The Raman spectra of carbonates are dominated by the symmetric stretching vibration ($\nu_1$) of the $CO_3$ group, which occurs at 1084 $cm^{-1}$ for calcite and at 1069 $cm^{-1}$ for monohydrocalcite, and is split into two (1090 and 1077 $cm^{-1}$) for vaterite owing to a lowering of symmetry and the resultant removal of the degeneracy of $CO_3^{2-}$ in the centro-symmetric calcite structure.[13–15] This distinct difference between the Raman spectra of monohydrocalcite and vaterite makes it possible to distinguish unambiguously between them.

In the spectrum of monohydrocalcite, $\nu_1$ (1069 $cm^{-1}$) can be clearly identified, but a strong fluorescence background masks the other weaker bands, and the only other features in the spectrum is a weak lattice vibration at 212 $cm^{-1}$ and traces of $\nu_2$ at 880 $cm^{-1}$.[14,15] The spherulites on which

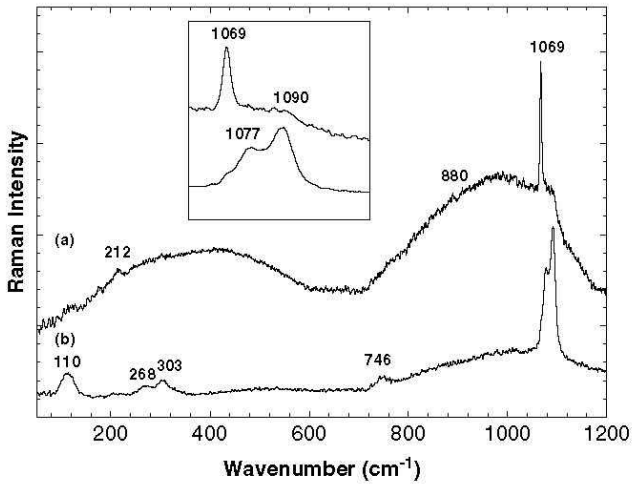


**Figure 2.** Raman spectra of rock hyrax urine: monohydrocalcite (a) and vaterite (b).

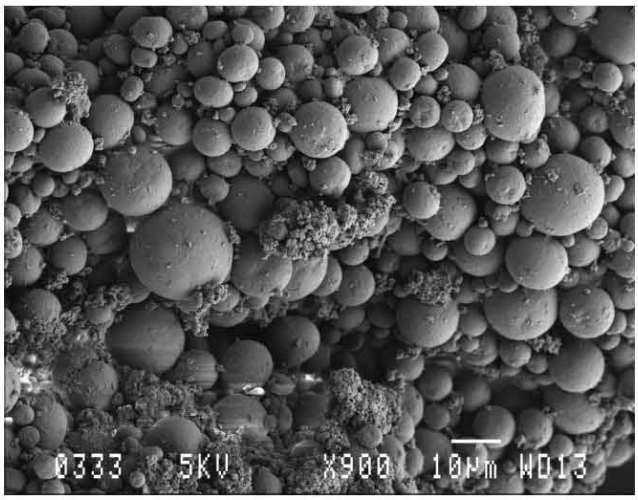


**Figure 3.** Electron micrograph of rock hyrax urine precipitates.

the vaterite spectra were recorded did not have this high background and $\nu_4$ can be seen at 746 $cm^{-1}$ as a small, broad band. The intensity is too low to observe the splitting that is characteristic for this band in vaterite spectra. Lattice modes are observed[13] at 110, 268 and 303 $cm^{-1}$. Vaterite and monohydrocalcite are known to crystallise with spherical morphologies. This is verified in the electron micrograph (Fig. 3) recorded of the urine precipitate. In fact it has become common practice to differentiate between vaterite and calcite using electron micrographs, as the rhombohedral calcite crystals are easily distinguishable from the vaterite spheres.[16–22] The morphology and size of the spheres, which varies between 0.1 and 30 µm, are consistent with reported literature values.[16–22]

The result was verified with XRD measurements (Fig. 4), which semi-quantitatively indicated that more or less equal amounts of vaterite and monohydrocalcite were present in this specific sample.

The transmission infrared spectrum of the crystallised hyrax urine recorded from the same KBr pellet used for the Raman measurements is shown in Fig. 5(b). The spectrum has features of both vaterite and monohydrocalcite. The $\nu_3$ vibration is split into two for both carbonates (vaterite: 1420, 1490; monohydrocalcite: 1406, 1485).[13] As the peak positions are close to each other, the two very strong bands at 1409 and 1485 $cm^{-1}$ (Fig. 5(b)) encompass these peaks for both carbonates and clearly distinguishes it from calcite (Fig. 5(a)), which has one $\nu_3$ band at ~1438 $cm^{-1}$. A clear indication of the presence of monohydrocalcite is the totally symmetric Raman mode ($\nu_1$), which is a forbidden mode in calcite and appears as a sharp peak (1069 $cm^{-1}$) superimposed on the split $\nu_1$ peaks of vaterite (1088 and 1070 $cm^{-1}$). The other peaks in the FTIR spectrum of monohydrocalcite occur at 580, 699, 762 and 873 $cm^{-1}$ and are all observed in the spectrum in Fig. 5(b).[13]

The spectrum in Fig. 5(a), identified as that of calcite with $\nu_3$ at 1438, $\nu_2$ at 873 and $\nu_4$ at 712 $cm^{-1}$, was recorded from a sample collected in the Karoo National Park, where the urine was not in contact with the faeces (visually observed as whiter in colour). In both FTIR spectra recorded of the

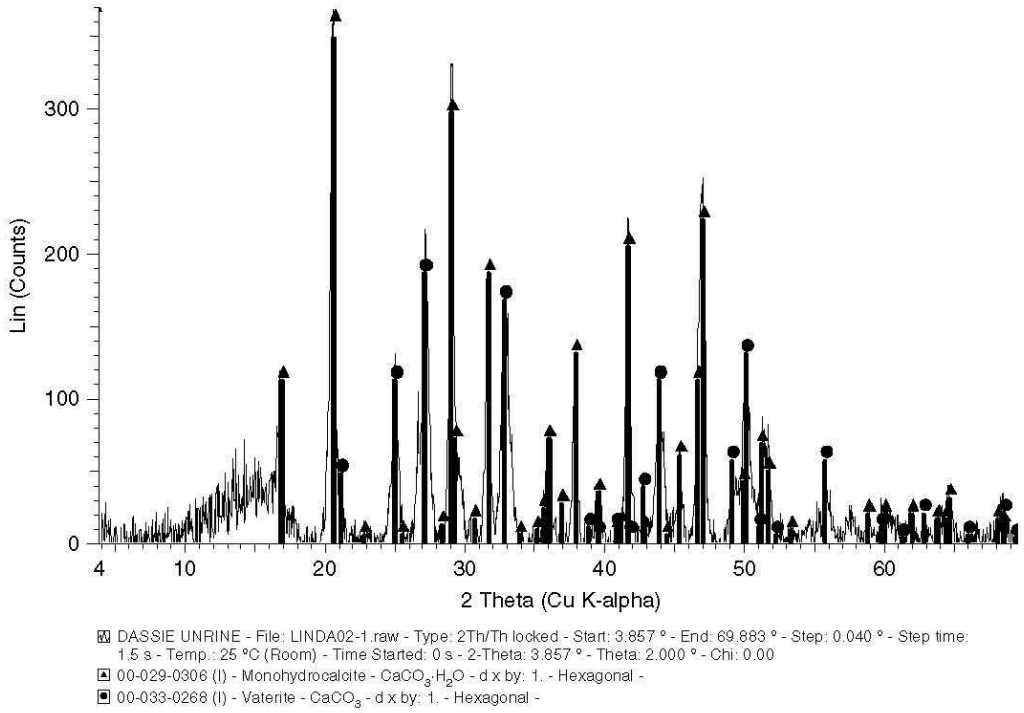


**Figure 4.** XRD spectrum of rock hyrax urine: ▲ = monohydrocalcite, ● = vaterite.

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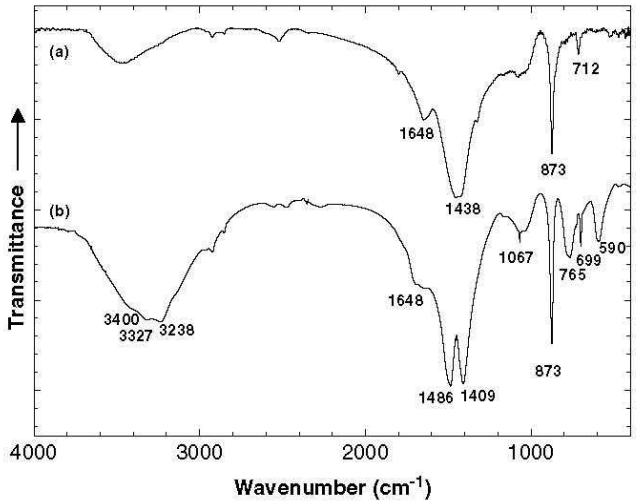


**Figure 5.** FTIR spectrum of rock hyrax urine (a) not in contact with faeces (calcite) (b) in contact with faeces (vaterite and monohydrocalcite).

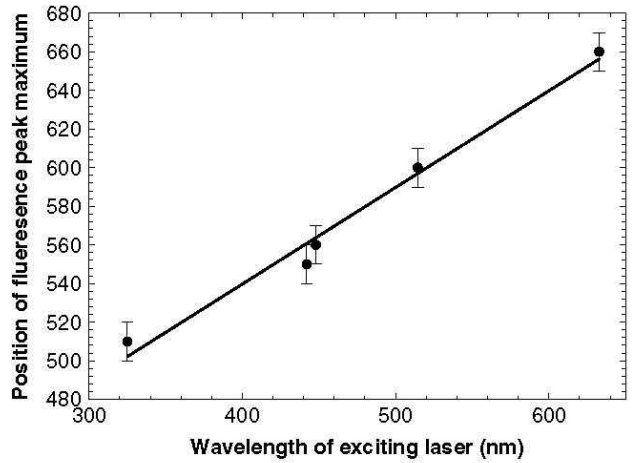


**Figure 6.** Wavelength of the exciting laser plotted against the position of rock hyrax urine fluorescence maximum.

urine, a band is observed around 1648 $cm^{-1}$, which indicates the presence of an organic phase.

In the Raman spectra recorded of monohydrocalcite, a strong fluorescence background was observed. This motivated the recording of luminescence spectra of rock hyrax urine, using UV (325 nm and 441 nm), blue (488 nm), green (514.5 nm) and red (632.6 nm) lasers as exciting lines. In Fig. 6, the peak maximum of the fluorescence is plotted against the wavelength of the exciting laser and it is clear that a linear relationship exists. Thus, rock hyrax urine absorbs light over the whole spectrum and releases this energy with a shift to longer wavelengths. At this stage it is not clear if this phenomenon has any biochemical or biophysical significance, e.g. as cue for avian predators similar as found for the UV fluorescent urine of voles and some Australian mammals.[23,24]

Monohydrocalcite ($CaCO_3 \cdot H_2O$) was first made in the laboratory in 1930, and in 1959 the first mineral deposition was identified. It is a rare mineral found in the Shiowakka cold saline spring in Japan in summer and also in Germany, Russia and the Czech Republic. It has also been detected in guinea pig bladder stones and tiger-shark otoliths.[25] The occurrence of vaterite in nature is nearly as rare as that of monohydrocalcite and has only seldom been observed, for instance, in the roots of germinating chickpea seeds, otoliths of the coho salmon and in frozen shrimp shells.[26,27]

These two unstable carbonates revert to calcite in solution and upon heating. It is therefore quite remarkable that it remains stable in hyrax urine, which for some samples could be hundreds of years old. Furthermore, the urine is found on rocky outcrops, exposed to a huge variety of weather conditions. The first sample was collected in the Limpopo valley after weeks of temperatures above 38 °C and a heavy downpour the previous night. Later samples were collected in the Karoo National Park, situated in a very dry, arid region of South Africa, with day temperatures in the summer often soaring to 40 °C and dropping to below freezing in winter. Fresh samples (similar spectrum as Fig. 5(b)) were scraped off rocks in the rock hyrax enclosure at the National Zoological Garden, which is regularly hosed down. As calcite is obtained for samples not in contact with the faeces, it is suspected that a growth controlling and stabilising agent is present in the faeces.

## Hyraceum

A sample of the fossilised urine and faeces mix (hyraceum) was obtained from Richmond, Karoo, Western Cape Province, in order to attempt to identify the growth controlling and stabilising agent. XRD analysis identified potassium chloride as the main inorganic component, with traces of vaterite, calcite, weddelite (calcium oxalate dihydrate), quartz and acetamide. It was not possible to record a Raman spectrum owing to excessive fluorescence of the organic phases, and only the FTIR spectrum (Fig. 7) of hyraceum could be obtained. A strong band in the OH stretch region (3100–3500 $cm^{-1}$) and two strong bands centred around 1601 and 1408 $cm^{-1}$ dominate the spectrum. The broad bands mask any characteristic bands that may be present of the large variation of aromatic amides, amines, alcohols and acids that have been identified by preliminary GC-MS analyses. Natural musk was also identified as a component. Identification of specific compounds is thus impossible, using only the FTIR spectrum.

## Syngenite detected on cave walls

Most spectra of the salty deposits collected on cave walls consisted of a mixture of bands that could belong to nitrates, sulfates or phosphates, and especially the broad bands typical of FTIR spectra could not be unambiguously assigned. It was possible though, to identify the relatively rare sulfate double salt syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$), as seen in Fig. 8(a),

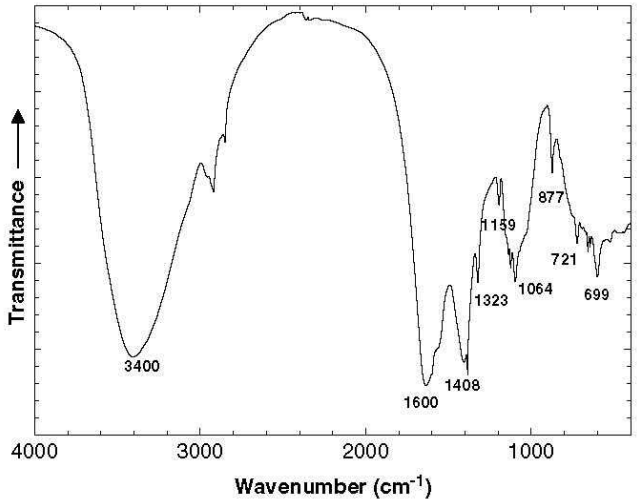


**Figure 7.** FTIR spectrum of hyraceum.

on one of the shards. The salt could not be separated visually from polyhalite, its co-precipitate as determined with XRD measurements and in many of the recorded spectra features of both salts were observed.

On the basis of the $C_s$ point group symmetry for the sulfate groups in syngenite, 18 possible Raman modes have been predicted. The two strong bands at 981 and 1005 $cm^{-1}$ are ascribed to the $\nu_1$ modes of the two sulfate groups, which are not identical as the bond lengths and angles are different and the oxygens bonded to different cations. The weaker bands at higher wavenumbers 1081, 1120, 1140 and 1165 $cm^{-1}$ have been assigned to the splitting of the $\nu_3$ modes of both sulfate groups.[28] Four $\nu_4$ modes of the two sulfate groups are observed at 607, 619, 632, 641 and 661 $cm^{-1}$. These results agree with the reference given in Ref. 24. The four bands at 427, 440, 471 and 491 $cm^{-1}$ originate from the $\nu_2$ bending modes of the sulfate anions. Thus, 16 of the predicted 18 modes are observed in our room temperature spectrum. The shoulder of the 1005 $cm^{-1}$ band at 1013 $cm^{-1}$ belongs to the totally symmetric stretching vibration of polyhalite (Fig. 8(c)). This is deducted from the XRD data, which indicated that polyhalite was a co-precipitate with syngenite. Both these spectra could be distinguished from $CaSO_4 \cdot H_2O$ (Fig. 8(b)), the most common sulfate salt, which was also detected.

## Oxalates

The presence of rock hyraces were obvious at all the rock art sites in the Mapungubwe National Park, as large areas were covered with a smooth black coating, which becomes very slippery when wet and is attributed to rock hyrax occupation. An FTIR spectrum of this black layer is shown in Fig. 9(d), and strong characteristic bands at 1623 (anti-symmetric $CO_2$ stretch), 1315 (symmetric $CO_2$ stretch), 780 (in-plane deformation) and 518 $cm^{-1}$ ($CO_2$ wagging) identified calcium oxalate monohydrate.[29] Other bands in the

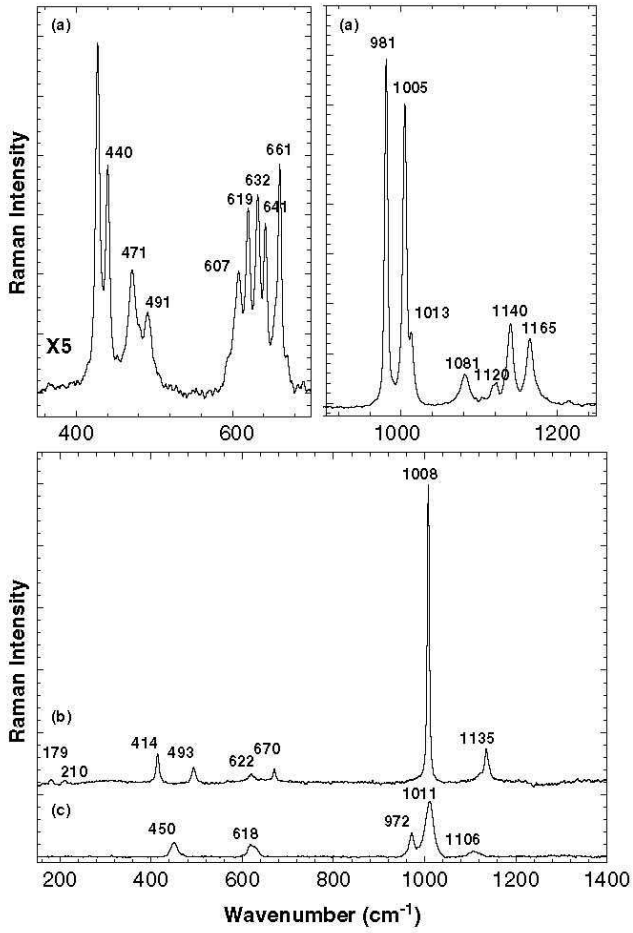


**Figure 8.** Raman spectrum of syngenite (a), gypsum (b) and polyhalite (c).

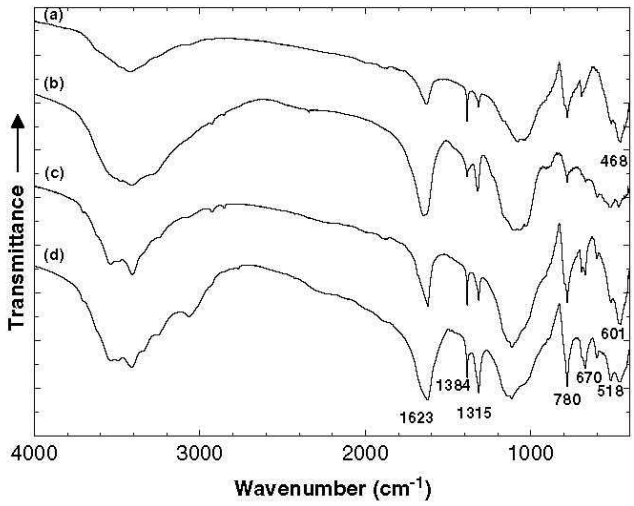


**Figure 9.** FTIR spectra of the salty deposits on cave walls (a–c) and (d) black layer covering cave floors, attributed to the occupation by rock hyraces.

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spectra are attributed to $\alpha$-quartz (broad band around 1090 and doublet at 798, 780 $cm^{-1}$) and possibly a nitrate (sharp peak at 1384 $cm^{-1}$, which varies in relative intensity and is also observed in the hyraceum spectrum). It is suspected that as the rock hyraces move around they cover the rocks with a mixture of urine, faeces and the glandular exudation of their feet.

Many of the salts collected on rock faces, where a clear sign of degradation was detected, also gave similar spectra of calcium oxalate monohydrate in varying concentrations (Fig. 9(a–c)).

Various studies have been conducted on encrustations on marble monuments and calcium oxalate mono- and dihydrate have been identified.[30,31] The presence of oxalic acid due to lichen populations are believed to be the origin of this phenomenon, but the exact mechanism is not fully understood yet.

## DISCUSSION

$CaCO_3$ is one of the most abundant minerals in nature and has importance in both geological and biological systems. The formation of $CaCO_3$ occurs naturally in seawater in organisms such as coral reef and mollusc shells, where it plays an important part in the immobilisation of carbon dioxide in the global environment. Calcium carbonate is also one of the main components of scaling, which has economic importance in the chemical engineering industry. It is also used in other industrial fields as an additive to medicines, foods, papers, plastics, printing inks, etc. Besides the hydrated salts (monohydrocalcite and hexahydrocalcite), three polymorphs of $CaCO_3$, namely, calcite, aragonite and vaterite, in order of stability and solubility, exist in nature. The crystallisation process and control of the formation of the different polymorphs and hydrated salts have been extensively studied.[16–22]

It has been found that amino acids, alcohols (e.g. ethanol, isopropanol, diethylene glycol) and magnesium ions promote the formation of vaterite.[16–22] In most studies supersaturated solutions also favoured the formation of vaterite and monohydrocalcite. It has also been reported that monohydrocalcite crystals have been grown from a complex saline solution of NaCl, KCl, $CaCl_2$, $MgCl_2$ and $NaHCO_3$, complemented with cell culture mediums and various biochemical additives.[14]

It would seem that the high concentrations of KCl and abundant organic molecules present in the urine/faeces mix of rock hyraces would in fact be ideal conditions for the formation of vaterite and monohydrocalcite. Furthermore, calcium ($CaCO_3$), phosphates, magnesium and urea are also present in rock hyrax urine.[2] Mg has been shown to promote the formation of vaterite,[19] and it has been established that orthophosphate ions inhibit the degradation of carbonates.[32]

A layered stone composed of predominately calcium and magnesium oxalate with a trace of phosphate has been found in the stomach of a wild hyrax.[2] This was attributed to the presence of plants high in oxalic acid in their diet, and as the breakdown of food in the hyrax digestive system is not as effective as for ruminants, oxalic acid may still be present in their metabolic products and thus provide a source for oxalate formation on rock faces.

## CONCLUSIONS

The weathering of the rock faces depicting San rock art are a complex mechanism encompassing interdependent mechanical, geological, chemical, physical and biological processes. Since 1994, ongoing studies monitor moisture and temperature changes in two caves in the KwaZulu Natal Drakensberg, and in 2003 step-scan XRD measurements were used to determine the depth of chemical changes in the Clarens Formation sandstone where weathering was observed.

The results of this first exploratory study, as to the possible use of Raman spectroscopy as a complementary technique in this project, have been extremely positive. It was possible to identify salts with microscopic resolution (between vaterite and monohydrocalcite) and also on a nanoscale (between syngenite and polyhalite). Raman spectroscopy will now be used to analyse the same samples used for the XRD measurements, and both results will be linked to temperature and moisture studies. The presence of rock hyraces, as well as bats, lichens and other plants and animals will be taken into account. Eventually, it is hoped to expand the project to include *in situ* Raman experiments, which will enable us to identify pigments (and perhaps binders) used in the paintings non-destructively.

The detection of the two rare carbonates in the urine instigated an awareness of the unique properties of hyraceum, which was used by early European settlers as well as indigenous people as traditional medicine. The Pharmaceutical University of Copenhagen is testing the validity of one of the medicinal properties ascribed to it, namely, as a cure for epilepsy, and some samples have tested positive.[32] Simultaneously, an extensive GC-MS study is under way to analyse the hyraceam fully and also to identify the volatile components of the faeces that might have the largest influence on the crystallisation processes on cave walls. As the composition of the hyraceum is dependent on the dietary intake of rock hyraces, samples from different environments will be compared (the samples used for the studies in Refs 4–6). This would provide a link to diet and composition of the urine and faeces.

### Acknowledgements

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