

Fourier-transform Raman spectroscopic studies of chronological change in stromatolitic cores from Antarctic lake sediments

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Abstract: The Fourier transform-Raman spectra of two lacustrine sediment cores from Antarctic sites are reported. The Lake Hoare specimens were predominantly calcium carbonate, quartz and β -carotene, with chlorophyll and calcium sulphate being noted as minor components. No evidence was found for iron (III) oxide or oxy-hydroxide bands. The Lake Nella specimens, in contrast, contain chlorophyll and quartz predominantly, but the absence of β -carotene is noteworthy. Here, the presence of haematite and a haematite–goethite mixture have been identified, with weaker features such as those of scytonemin, characteristic of cyanobacterial mats. The Raman spectra indicate that two different types of lake chemistry have been operating and several reasons are proposed for this.

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Key words: Antarctic, cyanobacteria, Fourier-transform Raman spectroscopy and lacustrine sediments.

Introduction

There is currently much interest in the biogeochemistry and survival strategies adopted by organisms exposed to stressed environments, such as the ‘cold deserts’ of the Antarctic. Sampling transects in Antarctica have revealed the response necessary for successful biochemical and biogeological combating of extremely low ambient temperatures ($< -60^\circ\text{C}$), low humidities ($\sim 0\%$) and high exposure to low-wavelength ultraviolet (UV) radiation resulting from atmospheric ozone depletion at high latitudes. Hence, epilithic lichens, chasmoliths and mosses are able to survive in continental maritime locations on the fringe of the ‘ozone hole’, whereas endoliths are found under the more extreme conditions in the colonization of sandstone in the McMurdo Dry Valleys. Similarly, the widespread occurrence of cyanobacterial mats of *Nostoc commune* in the littoral areas of seasonally and perennially ice-covered Antarctic glacial lakes has been attributed to the presence of scytonemin in the outer sheaths of the biofilms, which absorbs harmful UV radiation (Hodgson *et al.* 2001).

Raman spectroscopy has long been providing characteristic vibrational spectral information about the chemical composition of rocks and minerals, and several databases have been constructed that have assisted in non-destructive geological analysis of these materials. More recently, the ability of the Raman spectroscopic technique to identify biological and geological components in complex systems, without resorting to chemical extraction procedures, has enabled the structures of lichen encrustations and crypto-endolithic colonies to be mapped (Wynn-Williams & Edwards 2000). A particular advantage of the Raman technique in this application is the simultaneous recognition of signals from organic and inorganic chemical moieties; generally, metal oxides and sulphides, for example, have molecular vibrations that are found at low wavenumber shifts in the Raman spectrum (corresponding to absorptions in far-infrared spectroscopy). Although organic groups such as CH, CO, CC and CN have characteristic infrared wavenumbers, the identification of these modes in infrared spectra of a biogeologically modified endolithic community is hampered by the presence of broad absorption bands arising from OH modes.

The intrinsically weak Raman spectrum of water provides an excellent potential for the Raman spectroscopic study of

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lacustrine sediments; the sediment cores from ice-covered Antarctic lakes contain a historical temporal capsule of the geochemistry of the lake environment. Chemical information concerning the organic and inorganic components of a stromatolitic, lacustrine sedimentary core is essential to understanding the broader picture of the response of an organism to environmental changes. The aquatic habitat and inter-relationships between photosynthetic organic biomass in the lake and its destruction through bacterial redox processes involving metals such as iron and manganese, or ions such as sulphide and nitrate, is not a constant equilibrium. During stagnation (anoxic) periods in lacustrine systems, dissolved oxygen becomes depleted and redox processes can occur in which the organic biomass may be attacked by nitrate or sulphate. Sedimentation of insoluble salts or degraded biomolecules can then occur from the production of phosphates and sulphides from nitrate and sulphate reduction; precipitation of iron oxides, iron oxide-hydroxides, iron sulphides and manganese oxides results in anoxic conditions.

In the present study, we report on our Raman studies of the lacustrine sediments from two ice-covered Antarctic lakes, with a view to identifying the potential of Raman spectroscopy for the analysis of sediment cores for organic and inorganic materials.

Site description

Lake Hoare

Lake Hoare (77° 37' S, 162° 54' E) is a closed basin lake located in the McMurdo Dry Valleys. Among the dry valley lakes, it is relatively fresh, which has been suggested to be a consequence of it evaporating to dryness *ca.* 1200 yr BP and refilling since then (Lyons *et al.* 1998). The lake is fed by ephemeral glacial streams during 6–8 weeks in the summer. The lake is covered with 3–5 m of perennial lake ice, but a seasonal 'moat' does develop during the summer, allowing limited exchange between the lake and atmosphere in the summer. Sedimentation in the lake has been discussed previously (Anderson *et al.* 1993; Bishop *et al.* 1994, 1996; Doran *et al.* 1994a, b) and is characterized by heterogeneous fallout of sand-sized particles through cracks in the perennial lake ice cover, with a background settling of finer material, presumably washed in from the streams at the lake edges.

The bottom of Lake Hoare is characterized by microbial mats that are dominated by cyanobacteria in the shallow regions, and diatoms at depth (Hawes 1999). Brown alga is the other component of the mats. Carbonate layers are precipitated in the shallow regions of the lake, but not the deeper regions (Hawes 1999). Pigment analysis by high-performance liquid chromatography (HPLC) has been carried out on both surface sediments along a depth transect, and with depth in a sediment core and shows that the dominant pigments are carotenoids, chlorophyll and phycocyanin (Hawes 1999).

Lake Nella

Lake Nella (69° 24' S, 76° 22' E) is a seasonally open basin lake located in the Larsemann Hills, eastern Antarctica. It

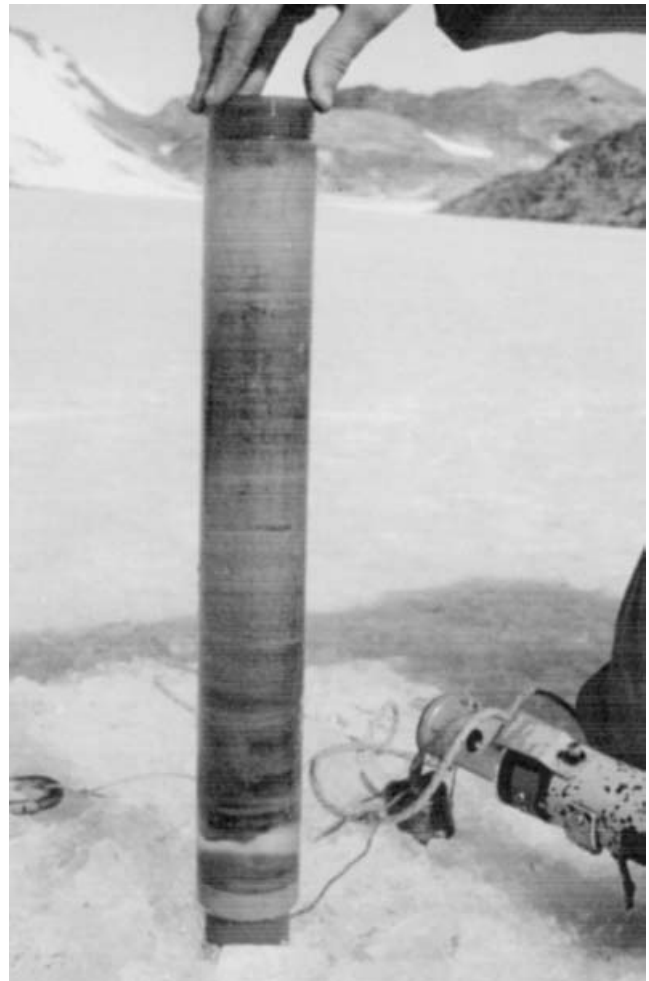


Fig. 1. Lake Nella sediment core (photograph).

was formed sometime before 1600 yr BP following the retreat of a remnant lobe of ice sheet, which occupied its catchment after the last glacial maximum (Hodgson *et al.* 2001). The lake is freshwater and is fed by a seasonal inflow originating from snowmelt and open lakes higher in the catchment. There is also an outflow stream that descends into Nella Fjord. Both streams flow for 2–3 months in the summer and have been estimated to transport up to $1 \text{ m}^3 \text{ s}^{-1}$ during peak periods (Gillieson *et al.* 1990). The lake is covered with *ca.* 2 m of lake ice, which partially melts each summer, allowing gas exchange between the lake and the atmosphere. The sediment core taken at 9.6 m water depth consists of finely layered 'stromatolitic' prostrate mats largely dominated by morphotypes of the genera *Leptolyngbya*, *Nostoc* and *Chondrocystis* with interstitial diatoms and green algae (Fig. 1). Minimal bioturbation (owing to the virtual absence of larger metazoa), limited wind-induced hydrodynamic mixing and slow decomposition rates are thought to contribute to the strongly laminated, well-preserved nature of these deposits (Vyverman *et al.*, in preparation). Inorganic material constitutes between 15 and 78% by weight (mean 61%) and is characterized by fallout of wind-blown sand-sized particles released into the water column during ice melting, forming

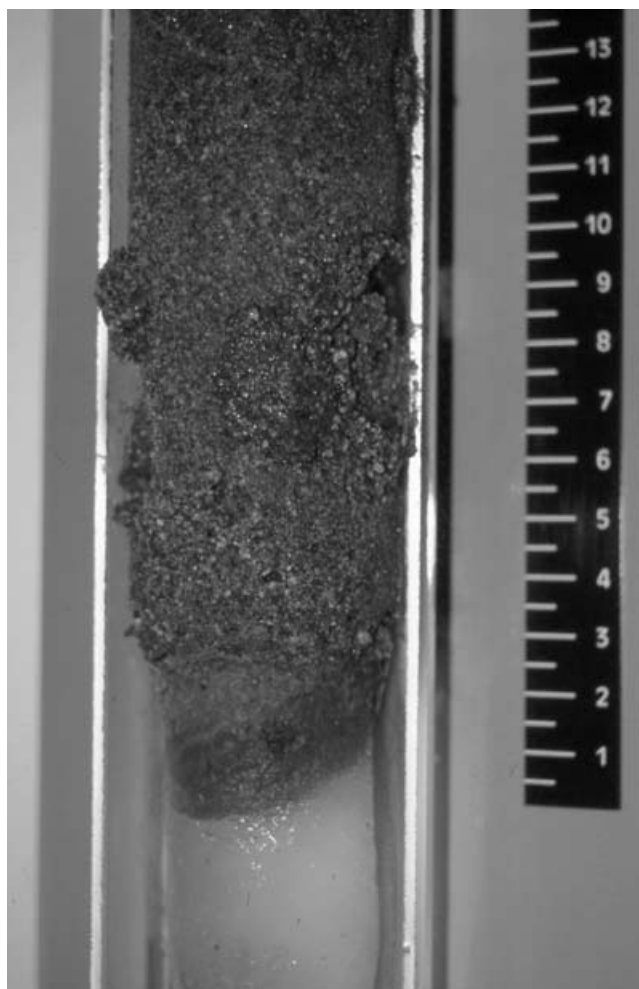


Fig. 2. Lake Hoare sediment core (photograph).

distinct sand layers, and finer material washed in by the inflow stream. Pigment analysis by HPLC has been carried out with depth in a sediment core.

Experimental

Specimens

Sediment cores were taken from 9.6 m depth in Lake Nella (Larsemann Hills) and ~15 m depth in Lake Hoare during field expeditions in the 1998 and 1999 seasons, respectively. The cores were visually very different in appearance: the Lake Nella core consisted of a series of coloured laminae (Fig. 1) extending over 32 cm. The Lake Hoare core (Fig. 2) was of a generally more uniform appearance, but with banded striations of red and green pigment occurring within 2 cm of its upper surface (the active microbial mat). Both lake cores were maintained at -10°C until required for study.

Raman spectroscopy

Fourier transform- (FT-) Raman spectra were recorded using the 1064 nm line of a $\text{Nd}^{3+}/\text{YAG}$ laser in the near infrared and a Bruker IFS66 instrument with an FRA 106 Raman

Table 1. Key inorganic Raman bands (cm^{-1}) for aquatic biogeological environments

Species/molecule	ν (cm^{-1})
Calcite, CaCO_3	1434, 1086, 712, 281, 156
Aragonite, CaCO_3	(1574, 1462), 1085, 907, 853 (721, 705) 284, 214, 161, 142
Whewellite, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	1492, 1468, 902, 503
Weddelite, $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	1474, 893, 498
Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1121, 1007, 662
Haematite, Fe_2O_3	1320, 613, 498, 412, (299, 293) 247, 225
Goethite, $\alpha\text{-FeO(OH)}$	993, 685, 550, 479, 385, 299, 243
Lepidocrocite, $\beta\text{-FeO(OH)}$	1303, 719, 650, 522, 493, 373, 245
Magnetite Fe_3O_4	663, 534, 513, 302
Maghemite, $\delta\text{-FeO(OH)}$	700, 500, 350
Pyrolusite, MnO_2	622, 610
Pyrites, FeS	279, 214
Quartz, SiO_2	465
Sulphur, S_8	490, 210, 150
Carbon, C	1590, 1320

module accessory. Spectra were accumulated over either 2000 or 4000 scans to improve the signal-to-noise ratio at a spectral resolution of 4 cm^{-1} and using a low laser power of nominally 25 mW to prevent damage to sensitive organic material in the core. A typical sample 'footprint' of about $100\text{ }\mu\text{m}$ is given in the macroscopic mode and wavenumbers of sharp bands are accurate to $\pm 1\text{ cm}^{-1}$.

Background to anoxic lacustrine sediments

The biogeochemistry of aquatic lacustrine sediments is a stationary state equilibrium between the production of organic algae biomass and its destruction in the habitat. Although there are numerous redox processes possible in an aquatic environment, relatively few elements are involved, including those considered 'essential' for life, namely C, H, N, O, P, S, and metallic elements such as Fe and Mn. The actual redox chemistry that applies in these situations is dependent on the microbiology of the system. During periods of stagnation, for example, concentration gradients of the essential elements for life processes can result. Hence, as dissolved O_2 is depleted relatively near the surface, other inorganic oxidant ions such as NO_3^- assume this role and can attack CO_2 and SO_4^{2-} ions dissolved in the water. At the sediment-water interface, the continual deposition of material coming out of solution is a critical factor. Within the first few millimetres of the sedimentation on the lacustrine bed, three major processes can apply – oxic (O_2 oxidation by dissolved oxygen), silboxic (reduction of nitrate ion and metal oxides) and anoxic (reduction of sulphate species and NH_4^+ , PO_4^{3-} , HS^- , CH_4 and HCO_3^-). In the presence of metal ions such as calcium, iron and manganese, a range of insoluble materials could be produced in sedimentary form, including FeS , $\text{Ca}_3(\text{PO}_4)_2$, FeO(OH) , CaCO_3 , MnO_2 and S_8 . In addition, organic moieties such as carotenoids, porphyrins and

Table 2. Raman band wavenumbers for Lake Hoare sediment core

Location of specimen*	Distance from core surface (mm)	Raman band wavenumbers (cm ⁻¹)
First red layer (a)	5	122mw, 180mw, 253w, 281m, 712w, 1008mw, 1087s, 1158m, 1463w, 1496w, 1523m
Second red layer (b)	10	122w, 156w, 281m, 713w, 1007vw, 1087s, 1158w, 1496w, 1521m
Green layer (c)	15	121m, 153w, 280m, 465w, 780mw br, 1007m, 1086s, 1158m, 1310m br, 1451w, 1523m, 1601w
Red layer (d)	20	121mw, 180w, 281m, 712w, 1087s, 1150w, 1495m, 1520mw
Middle sand (e)	70	126s, 160w, 201ms, 220w, 275w, 288w, 336ms, 396ms, 420w, 464s, 512s, 660m sh, 677s, 795w, 1007s, 1158w
Bottom sand (f)	150	120ms, 156s, 282s, 465m, 490mw, 510s, 713s, 790w, 1007w, 1087vs, 1436vw

* (a)–(f) indicated on the photograph of the core (Fig. 2).

Table 3. Raman band wavenumbers for Lake Nella sediment core

Location of specimen*	Distance from core surface (mm)	Raman band wavenumbers (cm ⁻¹)
Sample 5 (a)	50	120w, 465m, 507w, 1092m, 1132m, 1329ms br, 1457m, 2850m sh, 294s
Sample 10 (b)	100	125s, 203s, 256w, 365w, 440w, 464vs, 1120m br, 1330m br, 1459mw, 2850m sh, 2936s
Sample 15 (c)	150	120w, 399m, 1150w, 1300w, 2937m
Sample 20 (d)	200	125mw, 203m, 262w, 355w, 397w, 464s, 510w, 1072, 1329m br, 1460w, 1543w, 1591w, 2936s br
Sample 25 (e)	250	120w, 150w, 203w, 409w, 465m, 509m, 1089m br, 1328m br, 1457w, 2850m sh, 2933ms br

* (a)–(e) indicated on the photograph (Fig. 4).

chlorophylls can also be deposited along with the inorganics; spectroscopic studies of lacustrine sediments, therefore, can provide a chemical history of lake behaviour (Table 1).

Results and discussion

FT-Raman spectra were recorded of specimens removed from the stratified lake core samples removed whilst frozen; replicates were run to check for inhomogeneity. The results are presented in spectral stack plots over the wavenumber ranges 2600–3200 cm⁻¹ and 200–1700 cm⁻¹ for the Lake Nella and Lake Hoare sediment cores, respectively, in Figs 1 and 2 and band wavenumbers are given in Tables 2 and 3.

Lake Hoare analysis

The stratification comprises four distinct layers immediately at the surface of the core and underlying a permafrost ice layer; the coloured layers (a)–(d), were red, red, green and red. Specimens of the sandy-coloured core were also taken from the middle (distance from top of core 15 cm) and the bottom; these layers are labelled (e) and (f) in our classification in Table 2 and Fig. 2. The Raman spectra (Fig. 3) of the coloured layers show the presence of calcium carbonate and β -carotene in all, with characteristic bands, respectively,

at 281, 712 and 1086 cm⁻¹ and 1523, 1158 cm⁻¹. However layers (a), (b) and (d) are red in colour, whereas layer (c) is green; the presence of chlorophyll in (c), shown by a broad medium intensity feature at \sim 1310 cm⁻¹ indicates that the carotenoid pigment is being swamped by the presence of chlorophyll in this specimen. The geological signatures are also interesting in that calcium carbonate occurs everywhere in the pigmented layers, but the ‘middle sand’ specimen contains calcium sulphate only, with the $\nu(\text{SO}_4^{2-})$ mode evident as a strong band at 1007 cm⁻¹.

It is also noteworthy that no bands are assignable to iron (III) oxide or iron (III) oxyhydroxide in its several forms; namely goethite, lepidocrocite and maghemite, although several spectra show the presence of α -quartz particles, as expected, with its characteristic Raman band at 465 cm⁻¹.

Generally, then, we can conclude that the pigmentation in the Lake Hoare sediment core is attributable to organic molecules. Other possibilities such as the iron oxides are definitely excluded, whereas the signature of pyrites would be compromised by the presence of the medium to strong intensity of the calcium carbonate band at about 280 cm⁻¹.

Lake Nella analysis

The sedimentary core from Lake Nella is shown (Fig. 1) and the Raman spectra of the specimens in Fig. 4 and Table 3.

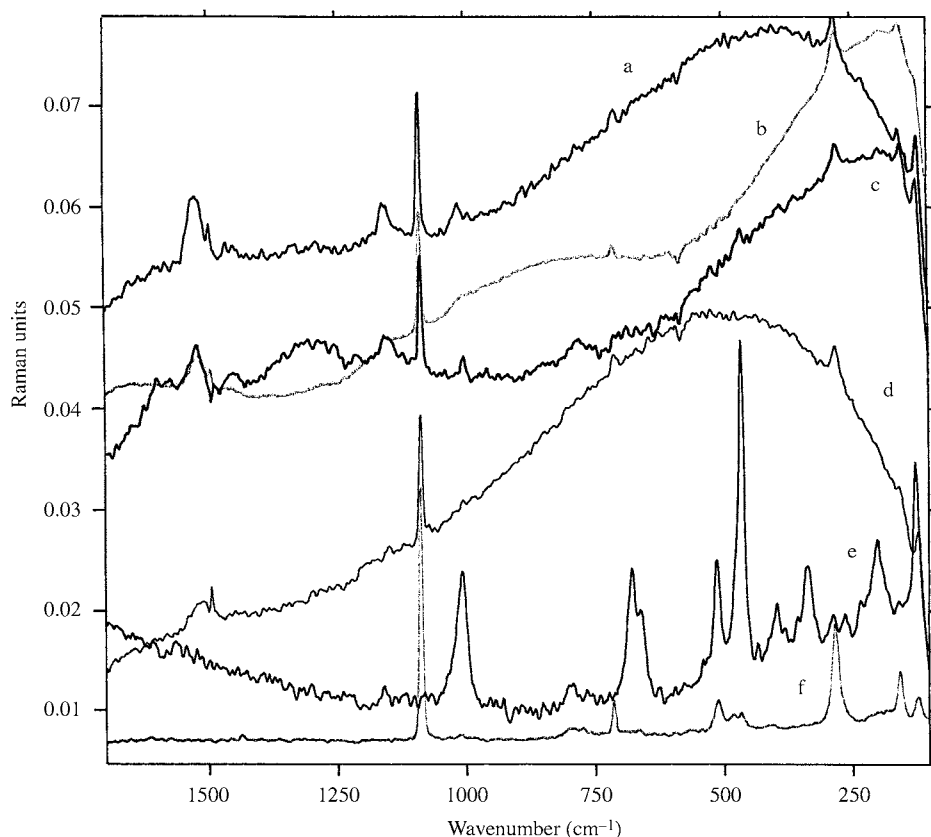


Fig. 3. FT-Raman spectral stack plot of Lake Hoare sedimentary core specimens (a)–(f); 1064 nm excitation; wavenumber range 100–1700 cm^{-1} ; spectral resolution 4 cm^{-1} , spectral scans accumulated, 2000.

Comparison of the Lake Nella and Lake Hoare cores shows that in the former there is much better preservation of discrete laminae over the length of the core and there is also a greater range of colours present. A microscopic examination of the stratified material indicated the presence of partly degraded filamentous cyanobacterial mats and inorganic minerals including sand layers. Previous characterization of the sediments using HPLC and HPLC-MS techniques has demonstrated that photopigments (carotenoids and chlorophylls) are present.

Benthic pigments were extracted from bulk sediments (*ca.* 1.5 cm^3) and analysed using HPLC following methods described in Hodgson *et al.* (1997) and Leavitt & Hodgson (2001). The main components were a KromaSystem 2000 HPLC with a Kontron pump, autosampler and diode array detector. The reverse phase columns used were 25 \times $\text{cm} \times$ 4.6 mm Spherisorb ODS-2 with a particle size of 5 μm . Pigment detection was at 435, 470 and 665 nm for all chlorophylls and carotenoids, with spectra from 30 to 700 nm being collected continuously. Solvent systems and operating conditions follow Wright *et al.* (1991). The output was calibrated to SCOR reference cultures (Jeffrey *et al.* 1997) and US Environmental Protection Agency Standards. Pigment derivatives were identified using a reference data set UV/visible spectra generated using HPLC (see Hodgson *et al.* 1997; Jeffrey *et al.* 1997; Airs & Keely 2000) and data on the

molecular mass and characteristic fragmentation patterns of pigments generated using 'off-line' and 'continuous-flow' HPLC-MS and MS methods (Hodgson *et al.* 1997; Airs & Keely 2000).

Table 4 shows the concentrations of pigments and pigment derivatives in selected sediment samples from the Lake Nella sediment core. Pigment concentrations are expressed as organic matter specific concentration (ng g^{-1} total organic carbon (TOC)) because comparison of long-term live plankton data with carved fossil records indicate that this metric most accurately captures variations in algal abundance and community composition. HPLC column retention times (rt) are given in minutes post-injection.

Five layers were selected from the core shown in Fig. 1 and the results of the Raman spectroscopic analysis are shown in Table 3 and Fig. 4; in particular, it should be noted that there is a progressive deepening of the red colour from samples 5, 10, through to green for samples 20 and 25. Sample 15 is typical of the core 'base' in that it is coloured dark green, presumably through degraded chlorophylls.

Although the Raman bands for the five Lake Nella specimens given in Table 3 are rich in features assignable to organic molecules, several important conclusions can be drawn from the Raman spectra and the presence or absence of characteristic biomarker bands.

Table 4. Table showing concentrations of pigments and pigment derivatives in selected sediment samples from the Lake Nella sediment core

Pigment	rt (min.)	Depth (cm)				
		5	10	15	20	25
Total carotenoids		4.375	0.512	0.310	0.000	0.101
Scytonemin reduced	7.13	0.216	0.252	0.310	0.000	0.101
Violaxanthin	11.15	0.047	0.172	0.000	0.000	0.000
Myxoxanthophyll	14.3–14.64	3.275	0.000	0.000	0.000	0.000
Nostoxanthin	17.4	0.142	0.000	0.000	0.000	0.000
Echinenone	22.22	0.694	0.089	0.000	0.000	0.000
Total chlorophylls		3.019	19.822	1.085	1.200	0.453
Chlorophyll <i>a</i> deriv. 1	5.09	0.000	0.000	0.995	0.474	0.440
Chlorophyllide <i>a</i> deriv.	7.4	0.000	0.305	0.000	0.000	0.000
Phaeophytin <i>b</i> deriv.	8.01	0.000	2.762	0.000	0.000	0.000
Chlorophyll <i>a</i> deriv. 2	8.29–8.44	0.000	2.307	0.000	0.057	0.000
Phaeophytin <i>a</i> epimer	9.36–10.25	0.697	4.278	0.000	0.102	0.000
Phaeophytin <i>a</i> epimer	10.9	0.000	1.380	0.000	0.018	0.000
Pyropheophytin <i>a</i>	13.29	0.615	0.000	0.090	0.000	0.000
Phaeophytin <i>a</i> epimer	13.92	0.224	0.000	0.000	0.000	0.000
Pyropheophytin <i>b</i>	20.68	1.058	3.480	0.000	0.231	0.000
Phaeophytin <i>a</i> epimer	20.94–21.1	0.000	3.180	0.000	0.214	0.000
Phaeophytin <i>a</i> epimer	21.46–21.85	0.000	0.730	0.000	0.041	0.000
Pyropheophytin <i>a</i>	22.68–23.23	0.000	0.269	0.000	0.000	0.000
Pyropheophytin <i>a</i>	23.39–24.59	0.425	1.131	0.000	0.062	0.013

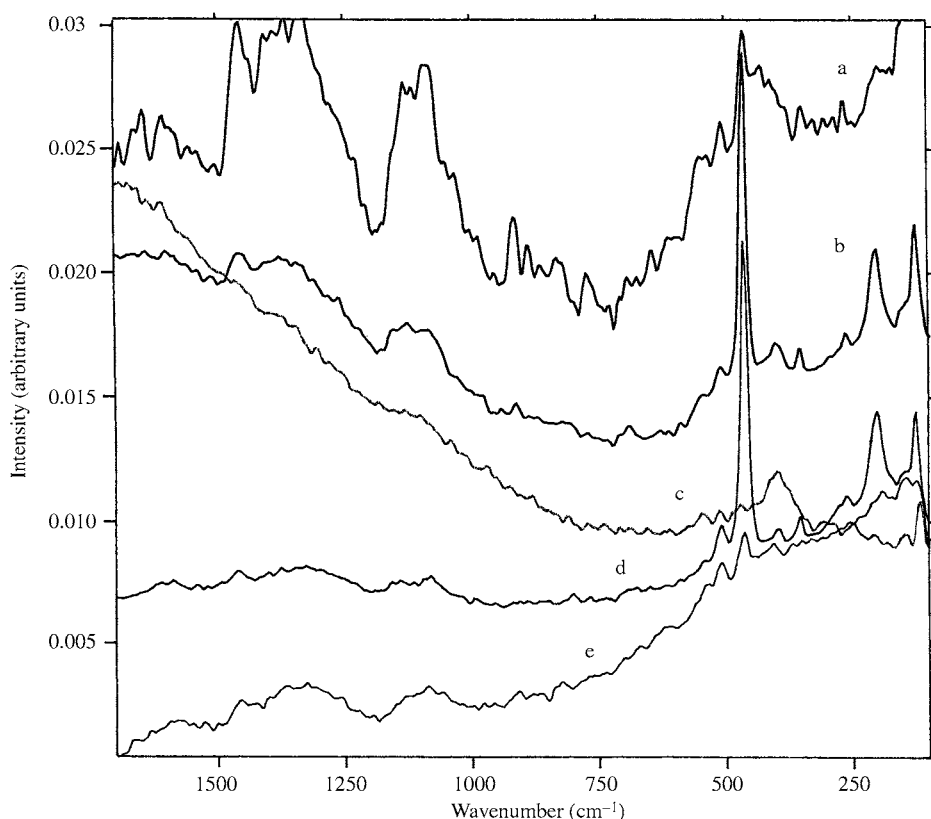


Fig. 4. FT-Raman spectral stack plot of Lake Nella sedimentary core specimens; (a)–(e); conditions as in Fig. 3.

- The markers for chlorophyll and associated organics occur in all five specimens; in particular, the broad feature near 1320 cm^{-1} and the $\nu(\text{CH})$ stretching modes near 2900 cm^{-1} .
- There is no evidence for carotenoids in the spectra.
- The chlorophyll signal decreases in intensity from samples 5–10 to sample 15 and then increases again for samples 20 and 25. This suggests that there is a progressive chlorophyll

decrease in the first three specimens and confirms that the core 'base' is composed of chlorophyll residues. In another study of the senescence of Antarctic snow algae, the decrease in chlorophyll from the green to red regions has been noted in the Raman spectra.

- α -quartz appears in four of the samples studied, but not in sample 15.
- Unlike the Lake Hoare core sediment study, several of the specimens here show bands in the low-wavenumber region characteristic of inorganic oxide pigments; in particular, attention can be drawn to bands near 400 and 300 cm^{-1} , which are representative of iron (III) oxides and oxyhydroxides in the haematite–goethite–lepidocrocite–maghemite system. Sample 25, for example, has a weak feature clearly belonging to haematite at 409 cm^{-1} , whereas samples 15 and 20 have a band near 397 cm^{-1} , which is better described as a haematite–goethite, mixed composition. There is no evidence for iron oxides in samples 5 and 10.
- Calcium carbonate/aragonite is not evident in any samples, because despite a signal observed near 1080 cm^{-1} , the supporting band at 281 cm^{-1} is absent; we conclude, therefore that the 1080 cm^{-1} feature is ascribable to an organic pigment containing CO groups such as a phycocyanin. This is supported by HPLC detection of phycobiliproteins in the sediments of adjacent lakes. Several weak bands in the spectra of specimens 5–25 can be suggested as belonging to materials such as scytonemin (1591, 1543 cm^{-1}) and quinones (1460 cm^{-1}).

We therefore conclude that the Lake Nella specimens are richer in organics than those of Lake Hoare, but also note that the former specimens have a clear indication of a mineral pigment composition based on the iron (III) oxide–oxyhydroxide system. No evidence is found for gypsum, pyrites or calcite in the Lake Nella samples, but a weak feature near 500 cm^{-1} indicates sulphur, which probably results from anoxia caused by periods where there is multi-year ice cover and no annual melt. Alternatively, it could be the result of anoxia in the deeper layers of sediment, which is often associated with sulphate-reducing bacteria.

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