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CLAY AEROSOLS AND ARCTIC ICE ALGAE

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Abstract—The red snow algae species found in snow at Resolute, Canadian Arctic, is a unicellular *Chlamydomonas nivalis*. Investigations by SEM-EDX, TEM, FT-IR, GC and GC-MS suggest that clay aerosols may provide nutrients for these unique systems. The clays provide P, S, K, Si, Ca, and Mg. Soot is also present and halite is very common. This salt probably plays a significant role in lowering the freezing temperature. The red snow algae is coated by a sticky thin film composed of both organic membrane material and inorganics consisting of mica and smectite. Green algae rich in Ca are involved in active photosynthesis while red algae are in a resting stage. Protamine, stearic acid, and decanoic acid were found at Ca-rich green cells while carminic acid and nopalcol BR-13 were found at Ca-poor red cells. The cell wall of red algae is composed of protein with cellulose. The major fatty acides in cells are all of even-carbon species with maximum concentrations of palmitic acid, stearic acid, and behenic acid, suggesting normal chemistry of algae species without C22. High concentration of n-alkanes with n-C24 is a characteristic component in this red snow algae, suggesting the presence of hydrocarbons that could be derived from the Arctic cold desert and/or organic debris of wind-transported bacteria. It is likely that such organic and inorganic matter provide the nutrient sources for the red snow algae in ice.

Key Words—*Chlamydomonas nivalis*, Clayey aerosols, Electron microscopy, Fourier transform infrared, Gas chromatograph mass spectrometer, Red snow algae.

INTRODUCTION

Green and red snow algae from Antarctica have received extensive attention (Kol, 1968, 1969; Fritsch, 1911; Matsumoto *et al.*, 1990; Akiyama, 1974, 1975, 1979, 1981, 1985, 1990; Akiyama *et al.*, 1988, 1989, 1990; and Fogg, 1967. Red snow algae have been described from both Antarctica and the arctic (Newton, 1982; Nicholas *et al.*, 1990), North Finland (Kol and Eurola, 1973, 1974), east Greenland (Fjerdingstad *et al.*, 1974; Koshima, 1991), the Alaskan arctic (Kobayashi, 1967), and Japan (Fukushima, 1963; Kobayashi and Fukushima, 1952). Most of the red snow algae species collected from various regions have been classified and determined as *Chlamydomonas nivalis* (*chlorophyceae; chlorophyta volvocales*) (Mosser *et al.*, 1977; Newton, 1982; Fjerdingstad *et al.*, 1974; Kobayashi, 1967). Red blooms of snow algae consisting almost exclusively of large spherical red cells of *Chlamydomonas nivalis* are widespread only during the summer months. Most samples photosynthesize optimally at 10° or 20°C but retain substantial activity at temperatures as low as 0° or −3°C. Exceptional samples photosynthesize optimally at 0° or −3°C (Mosser *et al.*, 1977). Blooms of algae are known to occur in snow when air temperatures remain above freezing for extended periods of time. Red snow algal blooms generally occur in brightly illuminated locations, while green, blue, or yellow blooms develop in more shaded positions and sometimes deeper in the snow. We found that both red and green snow algae are able to develop in similar open places in the arctic region.

Chemical analyses of red snow, *Chlamydomonas nivalis*, using proton-induced X-ray spectroscopy, revealed that elements such as Si, Al, Cl, Fe, Ca, and K occurred in the greatest concentration in the snow as well as in the algae. The accumulated concentrations of Mn, Cu, and Zn must be looked upon as the organism's need and tolerance for these trace elements. The pronounced Hematochrome development in the algae is the result of the great intensity of light (Fjerdingstad *et al.*, 1974).

Besides red snow algae, Antarctic soil was analyzed by Matsumoto *et al.* (1990) and the authors found unusual distributions of long-chain n-alkanes and n-alkenes, which could be derived from cyanobacteria and microalgae that live in the Antarctic cold desert. These investigations, and those on snow algae from various regions in the world, have been mainly biologic in nature, and little is known of the microbiochemical, biomineralogical, and environmental geologic factors for their growth.

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Red snow algae were much in evidence in Resolute, Canadian Arctic, during our visit in June 1991 and are the subject of the biomineralogical and biochemical investigations reported here.

MATERIALS AND METHODS

Sampling site and samples

Snow colored red by algae was found in permanent snowfields near Resolute, Cornwallis Island, near the magnetic north pole in the Canadian Arctic in June 22, 1991. The length of the day there is 24 hours. The red snow algae were collected from the Prospect hills, 200 m high, beside the Mecham River, which flows into Resolute Bay. The river water, 2.4°C and pH 8.1, flows through sedimentary rocks of limestone containing gypsum and phosphates. Aerosol dust was also collected by air-sampler on the same day in windy Resolute and found to contain clay minerals, sulfur, anhydrite, calcite, and halite. In the period of study, the air temperature varied from +3°C to −3°C at Resolute. The snowline was high, and only a few permanent snow banks remained. No new snow fell during the period of observations. Concentrations of red species were found only within the top centimeter of the snow.

Analytical methods

The snow algae sample was mounted on glass slides for optical observation and separation of red algae from green algae. Parts of the sample were mounted on a sample stub with double-sided tape and coated with carbon for scanning electron microscopy (SEM) equipped with energy dispersive X-ray analyzer (EDX), using a JEOL JSM-T220A instrument operating at 20 kV. Some samples were ground in a porcelain mortar, then clay-size fractions were transferred to a microgrid for high-resolution transmission electron microscopy (HRTEM), using a JEOL JEM 2000EX operating at 160 kV. The samples, after separation of red algae from green algae, were analyzed by Fourier transform infrared (FTIR) spectroscopy using both HORIBA FT-530 and JIR-MICRO6000 systems.

Crushed samples were separately analyzed for the cell wall (crust) and cell contents by FTIR. The samples were also extracted in a soxhlet extraction apparatus with benzene/methanol (9:1) for 24 h. The extracts were evaporated and subjected to preparative thin layer chromatography on silicic acid (KISELGEL 60 PF254, MERK) with elution by n-hexane to isolate saturated hydrocarbons. The analyses were programmed using a Shimadzu GC-14A gas chromatograph (GC) and QP 2000A gas chromatograph mass spectrometer (GC-MS) equipped with a 30 m × 0.25 mm i.d. fused silica capillary column coated with DB-5 (J & W). The oven was programmed from 40° to 300°C with a 4°C/min heating rate.

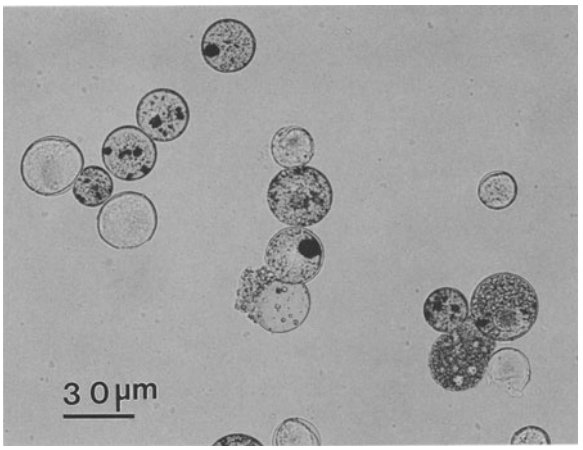


Figure 1. Optical micrographs of red and green snow algae, *Chlamydomonas nivalis*. Red cells are in the resting stage; green cells are in the photosynthetic stage.

RESULTS

Optical microscopy

Red and green unicellular algae wrapped in spherical cells with a diameter of 10-20 μm were found in the red snow sample (Figure 1). The red algae are predominant, with the green algae scattered among the red ones. Judging from color, size, and form, they are presumed to be the *Chlamydomonas nivalis*, a unicellular alga, as reported by Fukushima (1963) and Kobayashi (1967). They were in a resting stage with no cells in division stages, although some were oozing components outside through cracks on the cells.

Composition of snow algae

The composition of both red and green cells was analyzed by EDX as shown in Figure 2. The green cells are composed mainly of Si, P, S, and Ca with abundant organics showing a high background (Figure 2A). Red cells are composed of Si, P, and S with abundant organics without Ca (Figure 2B). There was a constant difference in Ca composition between the red and green cells, associated with the presence of Mg, Al, Si, P, S, Cl, and K components. Semi-quantitative chemical analyses of green and red cells indicate the difference of Ca content. Concentration of Ca in green cells is eight times more than in the red cells.

Relatively high Al, Si, K, and Fe contents were determined on the surface of the algae cell, which was coated by thin films (Figure 3). The thin films are composed mainly of inorganic materials showing low background. Jointed parts of cells were connected with films or tubes of alumino-silicate minerals composed of Mg, Al, Si, K, Ca, and Fe without any organics (Figure 4), suggesting smectitic and illitic clay components as shown in TEM lattice images. Both surface and junctions of the cells appear with rough surfaces of oily gelatinous

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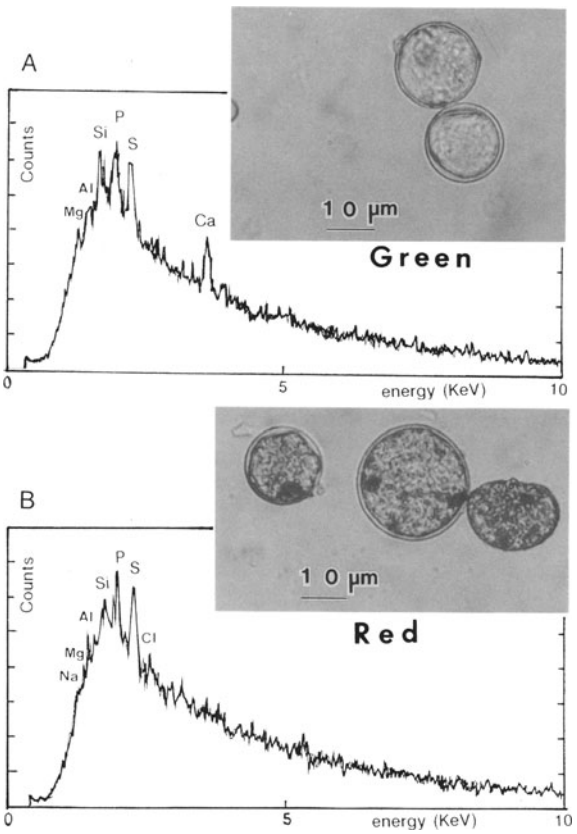


Figure 2. EDX analyses of A) the green snow algae cell, showing high Ca content; B) the red snow algae cell, showing little Ca.

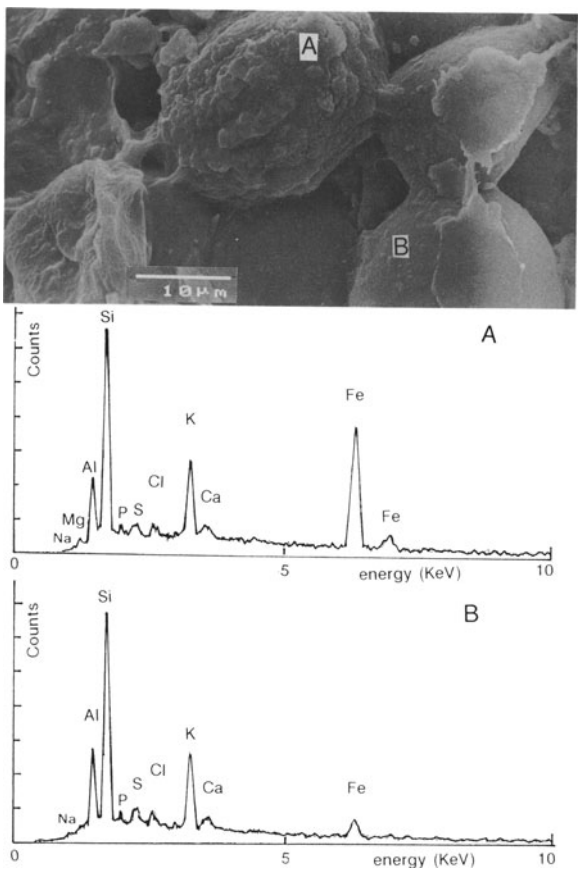


Figure 3. Scanning electron micrograph of snow algae, showing clayey dust thin films on the surface (with EDX chemical analyses).

aggregations characterized by high Si, Al, K, and Fe contents. Fe shows the greatest concentrations as shown in Figures 3A and 4.

Aerosol particles

TEM observation of ground samples revealed the presence of inorganic materials with soot which can be supplied by dust. Granular materials (Figure 5A), spherical soot (Figure 5B), and small oval bacteriophages or virus cells (Figure 5C) as reported by Fjerdingstad et al. (1974) were observed. The cell in the photosynthetic stage is surrounded by an undulate membrance about 170 Å in width. These particles were attached to their clay film (Figures 5B and 5C). HRTEM revealed that the thin films were crystalline with lattice images of 4.2, 4.5, 5.0, 8.3, and 10 Å (Figure 6). These d-spacings indicate that the thin films are composed of mica group minerals and smectite.

Dust samples collected by air filters at Resolute were found to contain sulfur, barite, gypsum, anhydrite, halite, calcite, clay minerals (14 and 10 Å) and carbon, and large amounts of amorphous materials both organic and inorganic (Tazaki *et al.*, 1992). Mineralogical components of clay aerosols on the snow algae are similar to air-filter dust samples.

Organic materials

FTIR was applied to determine microbio-organic chemistry for individual green and red cells that showed different compositions. Protamine, stearic acid, and decanoic acid were found in Ca-rich green cells, whereas carminic acid and nopalcol BR-13 were found with Ca-poor red cells (Figure 7). The chemical analyses of both green and red cells showed the mixture of shell and the inner cell contents. By using crushed samples, each specific element in the shell and the inner content can be determined. By focusing the IR beam on a region of the inner contents (MI-1), linear-hydrocarbon and unsaturated fatty acid chains were observed (Figure 8 upper). On the other hand, the outside shell (KARA-1) contained protein with cellulose (Figure 8 below) with very similar IR spectra patterns as shown in Figure 7 (red cell).

The lipid elements of the cell were determined using GC and GC-MS as illustrated in Figures 9 and 10. Fatty acid concentrations in the red snow algae were

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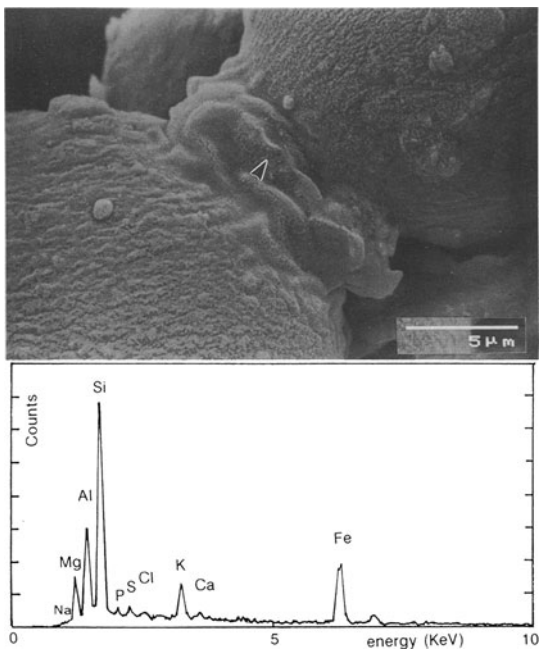


Figure 4. Scanning electron micrograph of joined parts of snow algae, showing smectitic and illitic clay components.

found, including palmitic acid (n-C 16:0) 49.5%, stearic acid (n-C 18:0) 10.8%, oleic acid (n-C 18:1) 5.6%, and behenic acid (n-C 22:0) 10.5%, showing all even-carbon numbered ester-form fatty acids. The major fatty acids in the red snow are similar in chemistry to normal algal species that contain only C 16:0 and C 18:0, but C 22:0 is at high concentrations in the red snow. It is known that bacteria contain no long-chain n-alkenes and n-alkanes with an odd-carbon predominance. Unexpectedly, quite high concentration of n-alkane maximized at n-C24, 67.4%, is also a characteristic component of the red snow algae. Before the measurements the sample weight was 21.8 mg and, after the soxklet extraction, the remainder of the sample was 10.7 mg, suggesting that almost half of the sample was of extractable organic matter. Ester-form fatty acids were present at a concentration of 274 μg /10.7 mg in the red snow sample. Free fatty acids were not detected. For comparison with ordinary algae samples, C 22:0 fatty acid and C 24 n-alkane are characteristic lipids in the red snow algae from Canadian arctic.

DISCUSSION

The SEM-EDX, TEM, FTIR, GC, and GC-MS analyses reveal that Si, Al, P, S, K, (Ca), Fe, and organics (ester-form fatty acids and n-alkane) are the major elements occurring in the greatest concentrations in red snow and in red snow algae, *Chlamydomonas nivalis,* at Resolute, Canadian arctic. P and S showed the greatest accumulated concentrations next to Si, suggesting

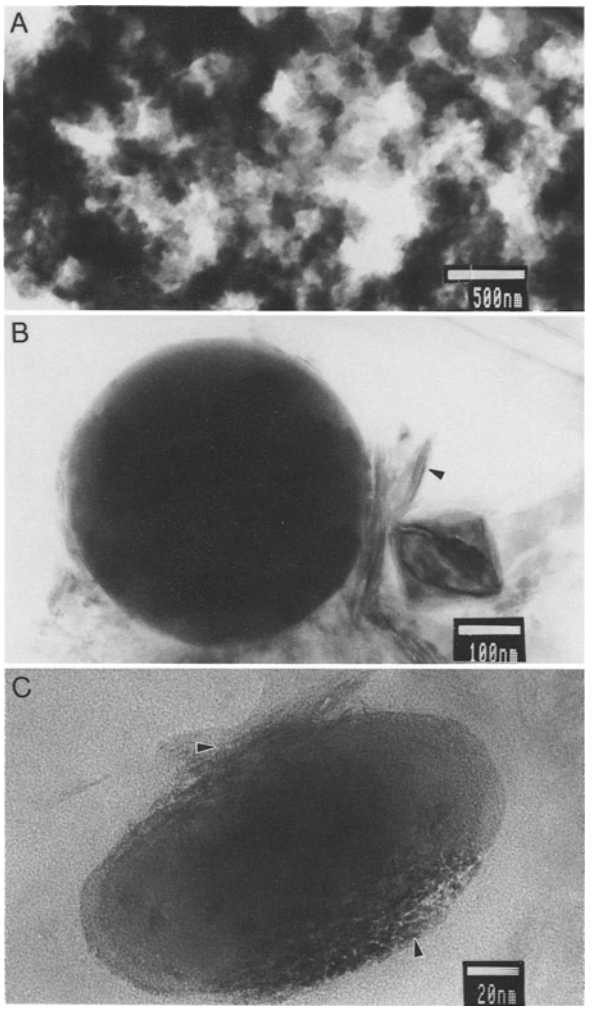
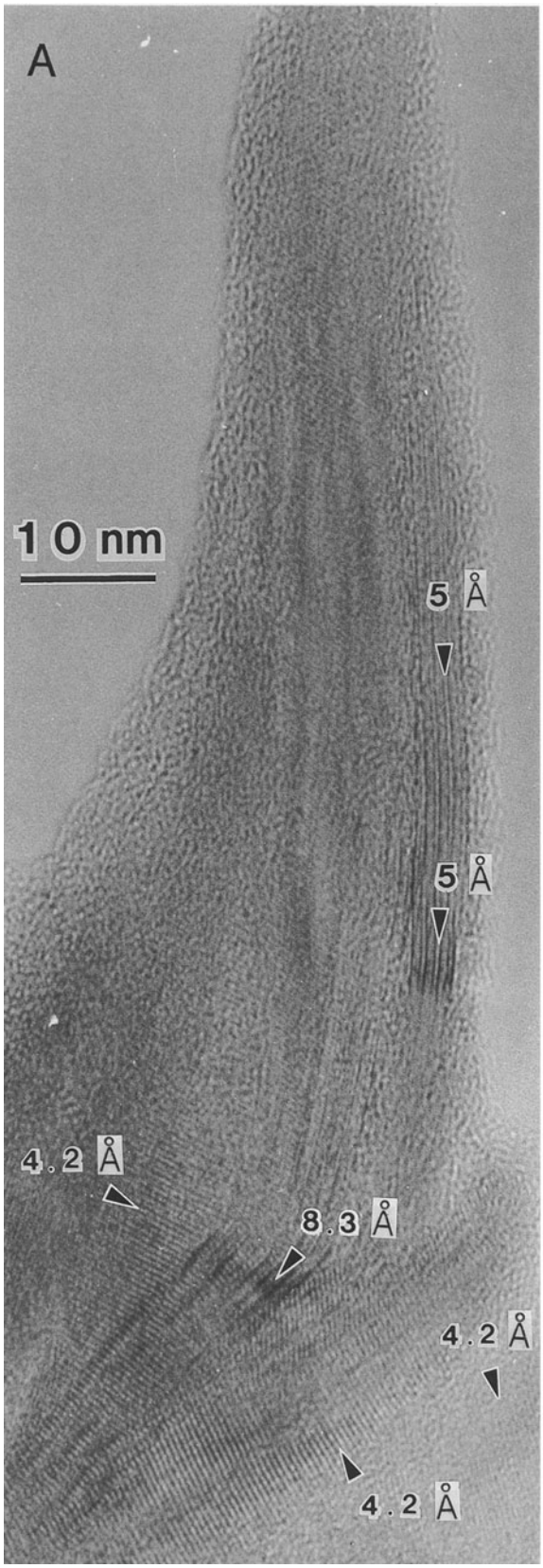
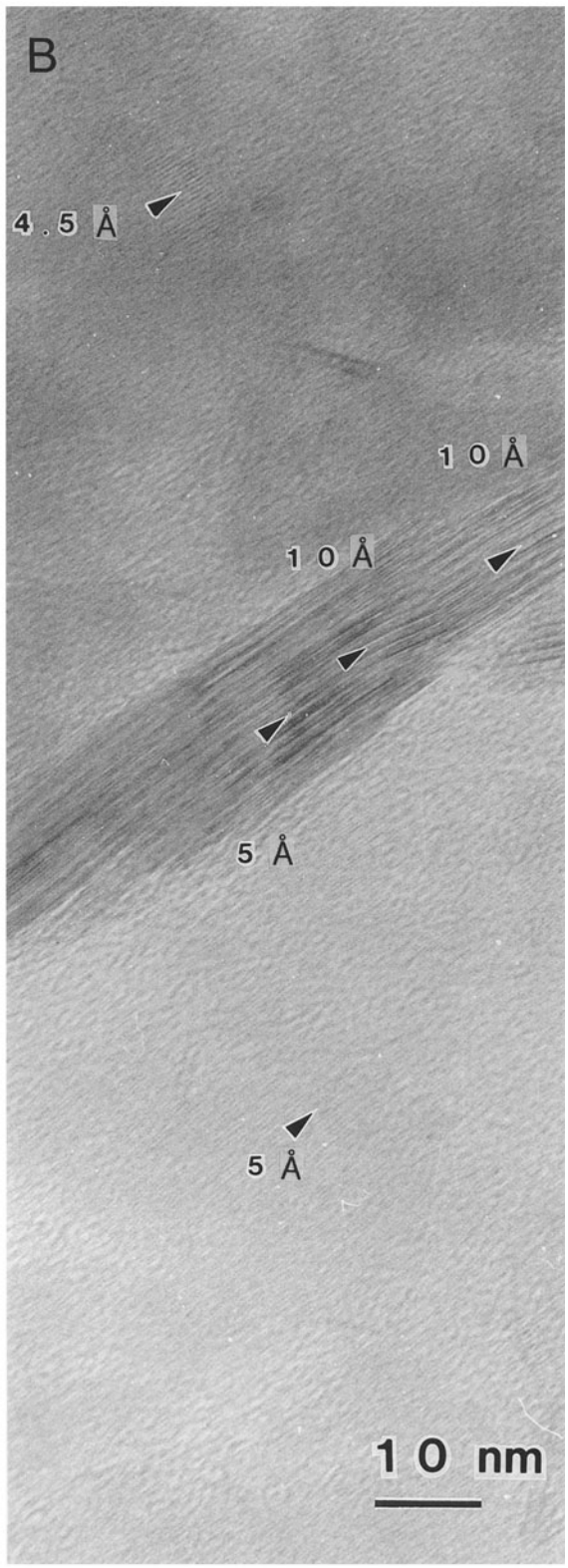


Figure 5. Transmission electron micrographs of snow algae showing A) granular materials, B) spherical soot, and C) oval bacteriophages or virus cells in the ground sample. Arrows in B and C indicate that clayey thin films attach to the surface.

that both P and S are of vital importance to the algae under conditions of such extreme low temperature. Numerous inorganic materials, including clay minerals, sediments, and rock debris, can be supplied from wind-borne dust, and the organisms may obtain N_2 from this dust (Fjerdingstad *et al.,* 1974; Koshima, 1991). Romanensko (1971) examined the photosynthesis of *Chlamydomonas nivalis* at Pamir and found that, during a 24 h period, the production of carbon in samples of red snow of one kilo each was 0.73, 0.50, 0.94, and 0.60 mg. Similarly, in Resolute, carbon in dust can be supplied by strong winds. Fatty acids of odd-carbon numbered in soil samples could be derived from cyanobacteria and microalgae, which lived in the Antarctic cold desert, and organic debris of wind-transported cyanobacterial mats (Matsumoto *et al.,* 1990). C 22:0 and C 24 in the red snow algae, which are not

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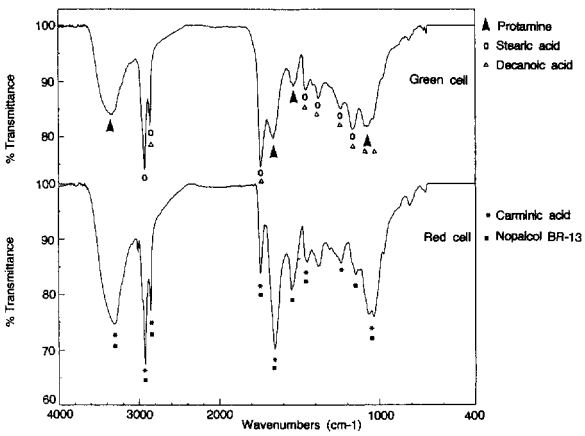


Figure 7. Fourier transform infrared of green and red snow algae, showing different organic components.

common in ordinary algae, suggest the different source materials. Such long-chain fatty acids and n-alkanes found in temperate lake or in marine sediments are explained by the input from vascular plant waxes and/or algae materials (Cranwell, 1973; Matsuda and Koyama, 1977a, 1977b, 1977c; Matsumoto *et al.,* 1990).

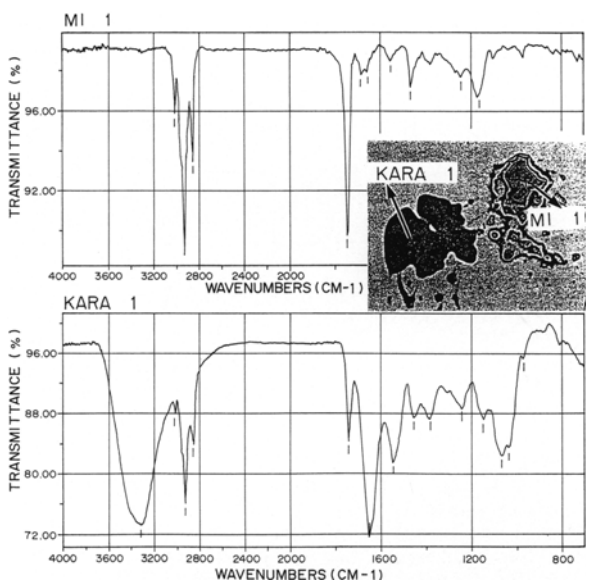


Figure 8. Fourier transform infrared of the inner content (M1) and the outside shell (KARA 1) of snow algae. The inner content is composed of hydrocarbons and fatty acids, whereas the outside shell is composed of protein and cellulose.

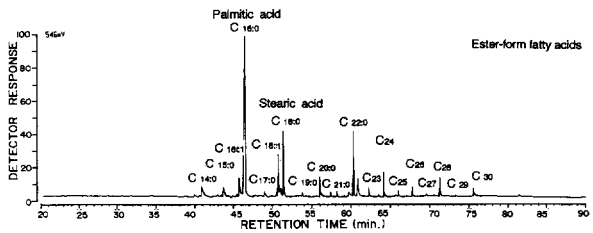


Figure 9. Gas chromatograms of red snow algae showing ester-form fatty acid components.

Aeolian transport of these elements from near or by long distance transport is possible. Anhydrite, barite, melanterite, and gypsum found in air samples at Resolute could come from local rocks. S, which is present in red snow algae, is believed to be derived from aerolian dust transport. Near-total depletion of the ozone in surface air is often observed in the Arctic spring, coincident with high atmospheric concentrations of inorganic bromine (Fan and Jacob, 1992). P can be supplied from surrounding limestones containing phosphate minerals. In the region of the Arctic, various organisms with dust may be buried under the ice sheets, a favorable condition for preservation of organic matter (Readman *et al.,* 1992; Sturges *et al.,* 1992). It is most likely that such organic matter and inorganic matter provide the nutrient sources for the red snow algae in ice.

CONCLUSIONS

Red snow algae species, *Chlamydomonas nivalis,* found on snow at Resolute, Canadian arctic, is composed of P, S, K, Si, Al, Ca, Mg, and organic materials. The red snow algal cell wall is composed of protein and cellulose, which is coated with thin films of clay minerals. Chemistry of the interior of the cell showed ester-form fatty acids and hydrocarbons. The results suggest that aerosols feed red snow algae on ice under

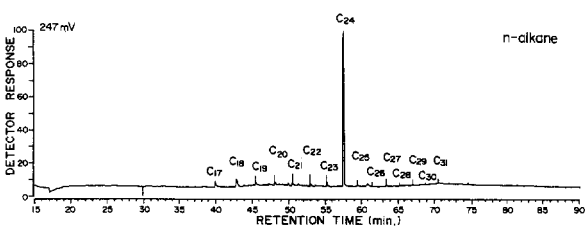


Figure 10. Gas chromatograms of red snow algae showing n-alkane components.

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Figure 6. High-resolution transmission electron micrographs of clayey thin films on the snow algal cell wall. The lattice images suggest that A) smectitic and B) illitic clay minerals are presented in the thin films.

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these cold conditions. Aerosols are one of the good nutrient sources for bacteria and contain high P, S, K, Si, Al concentrations. Soot materials and halite must be significant in lowering freezing temperatures in their biosystems.

REFERENCES

Akiyama, M. (1974) A preliminary note on some algae found in the ice-free area of the coastal region of Lutzow-Holm Bay: *Antarctica: Rept. Fac. Educ., Shimane Univ.* **8,** 37–50.

Akiyama, M. (1975) Plankton and bottom deposits of Lake Funazoko-ike in Skarvs Nes, Antarctica: *Rept. Fac. Educ., Shimane Univ.* **9,** 29–42.

Akiyama, M. (1979) Some ecological and taxonomic observations on the colored snow algae found in Rumpa and Skarvsens, Antarctica: *Proc. Symp. Terrestrial Ecosystem Syowa Atation Area, NIPR Spec. Issue* **11,** 27–34.

Akiyama, M. (1981) Algae in Antarctica: *Kyokuchi* **33,** 48–51 (in Japanese).

Akiyama, M. (1985) Biogeographic distribution of freshwater algae in Antarctica, and special reference to the occurrence of an endemic species of *Oedogonium: Mem. Fac. Educ., Shimane University* **19,** 1–15.

Akiyama, M. (1990) Notes on some southern Chilean soil algal flora: *Bull. Nat. Sci. Mus. B* **16,** 93–104.

Akiyama, M., Hayashi, M., Matsumoto, G., and Miura, K. (1990) Plant remains and related substances in the past lacustrine sediments of the Mt. Riiser-Larsen area, Enderby Land, east Antarctica: *Proc. NIPR Symp. Polar Biol.* **3,** 207–217.

Akiyama, M., Kanda, H., and Ohtani, S. (1989) Allelopathic effects of Antarctic lichen and mosses on the growth of algae: *Proc. NIPR Symp. Polar Biol.* **2,** 220–222.

Akiyama, M., Ohtani, S., and Kanda, H. (1988) Allelopathic interactions as a possible determinant in the structure and composition of Antarctic plant communities: *Polarforschung* **58,** 279–284.

Akiyama, M., Ohtani, S., and Kanda, H. (1991) Vertical distribution of Antarctic soil algae by direct observation with the contact slide method: *Proc. NIPR Symp. Polar Biol.* **4,** 183–185.

Cranwell, P. A. (1973) Chain-length distribution of n-alkanes from lake sediments in relation to post-glacial environmental change: *Freshwater Biol.* **3,** 259–265.

Fan, S. M. and Jacob, D. J. (1992) Surface ozone depletion in Arctic spring sustained by bromine reactions on aerosols: *Nature* **359,** 522–524.

Fjerdingstad, E., Kemp, K., Fjerdingstad, E., and Vanggaard, L. (1974) Chemical analyses of red "snow" from East-Greenland with remarks on *Chlamydomonas nivalis (Bau.) Wille: Arch. Hydrobiol.* **73,** 70–83.

Fogg, G. E. (1967) Observations on the snow algae of the south Orkney Islands: *Phil. Trans. Royal Soc. London B* **252,** 279–322.

Fritsch, F. E. (1911) Freshwater algae collected in the south Orkneys: *J. Lim. Soc. Bot.* **11,** 293–338.

Fukushima, H. (1963) Studies on cryophytes in Japan: *J. Yokohama Mun. Univ.* **C-43,** 1–144.

Kobayashi, Y. (1967) Coloured snow with *Chlamydomonas nivalis* in the Alaskan Arctic and Spitsbergen: *Bull. Nat. Sci. Mus.* **10,** 208–210.

Kobayashi, H. and Fukushima, H. (1952) On the red and green snow newly found in Japan I: *Report of Bot. Mag. Tokyo* **65,** 765–766.

Kol, E. (1968) Kryobiologie; Biologie und limnologie des schnees und eises: *E. Schweizerbart'sche Verlagsbuchhandlung (Nagele u. Obermiller),* 1–204.

Kol, E. (1969) The red snow of Greenland. II: *Acta Botanica Academias Scientiarum Hungaricae, Tomus* **15,** 281–289.

Kol, E. and Eurola, S. (1973) Red snow in the Kilpisjarvi Region, North Finland: *Astarte* **6,** 75–86.

Kol, E. and Eurola, S. (1974) Red snow algae from Spitsbergen: *Astarte* **7,** 61–66.

Koshima, S. (1991) Aerosols and ice algae: In *Chinese Loess,* Nagoya University ed., Kokon Press Comp. Tokyo, Japan, 290–299.

Matsuda, H. and T. Koyama (1977a) Positional isomer composition of monounsaturated fatty acids from a lacustrine sediment: *Geochim. Cosmochim. Acta* **41,** 341–345.

Matsuda, H. and T. Koyama (1977b) Early diagenesis of fatty acids in lacustrine sediments: I. Identification and distribution of fatty acids in recent sediment from a freshwater lake: *Geochim. Cosmochim. Acta* **41,** 777–783.

Matsuda, H. and T. Koyama (1977c) Early diagenesis of fatty acids in lacustrine sediments: II. A statistical approach to changes of fatty acid composition from recent sediments and some source materials: *Geochim. Cosmochim. Acta* **41,** 1825–1835.

Matsumoto, G., Akiyama, M., Watanuki, K., and Torii, T. (1990) Unusual distributions of long-chain n-alkanes and n-alkenes in Antarctic soil: *Org. Geochem.* **15,** 403–412.

Mosser, J. L., Mosser, A. G., and Brock, T. D. (1977) Photosynthesis in the snow: The alga *Chlamydomonas nivalis* (Chlorophyceae): *J. Phycol.* **13,** 22–27.

Newton, A. P. W. (1982) Red-coloured snow algae in Svalbard—Some environmental factors determining the distribution of *Chlamydomonas nivalis* (Chlorophyta volvocales): *Polar Biol.* **1,** 167–172.

Nicholas, J. B., Knoll, A, H., and Swett, K. (1990) A bangiophyte red alga from the proterozoic of Arctic Canada: *Science* **250,** 104–107.

Readman, J. W., Fowler, S. T., Villeneuve, C. C., Oregioni, B., and Mee, L. D. (1992) Oil and combustion-product contamination of the Gulf marine environment following the war: *Nature* **358,** 662–664.

Romanensko, V. L. (1971) Photosynthesis of algae in the red snow in Pamir: *Akad. Nauk. S.S.S.R. Informat. Bull. Akad. Nauk SSSR* **12,** 8–9.

Sturges, W. T., Cota, G. F., and Buckley, P. T. (1992) Bromoform emission from Arctic ice algae: *Nature* **358,** 660–662.

Tazaki, K. (1992) Electron microscopic observations of aerosol dusts from Kwait, China, Canadian Arctic circle and Japan: *Proc. 2nd Symp. Geo-Environments,* 113–118. The Committee of Environmental Geology ed., Geological Society of Japan.

Tazaki, K., Iizumi, S., Miyake, Y., and Goto, M. (1992) Observation on the nature of dusts from the Arctic circle in Canada: *Geol. Rept. Shimane Univ.* **11,** 13–24.

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